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Chemistry of Iminofurans: VI.* Synthesis and Structure of 2-(2-Ylidenehydrazino)-Substituted 4-Aryl-4-oxobut-2-enoic and 5,5-Dimethyl-4-oxohex-2-enoic Acids

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Abstract—Hydrazones derived from substituted benzophenones and fluorenone reacted with 4-aryl-2-hydroxy-4-oxobut-2-enoic and 2-hydroxy-5,5-dimethyl-4-oxohex-2-enoic acids to give the corresponding 2-(2-ylidenehydrazino) derivatives which may be used as initial compounds for the synthesis of 3-hydrazono-3*H*-furan-2-ones. The obtained but-2-enoic and hex-2-enoic acid derivatives in solution may exist as *Z*- and *E*-isomeric enehydrazine tautomers or hydrazone tautomers with *syn* or *anti* orientation of substituents with respect to the double C=N bond.

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We previously showed that 4-aryl-2-hydroxy-4-oxobut-2-enoic acids **I** react with benzophenone hydrazone and benzil monohydrazone to give the corresponding 2-(2-methylidenehydrazino)-substituted derivatives with *Z* configuration at the double C=C bond. The products were found to exist in polar solvents as 4-aryl-2-(methylidenehydrazono)-4-oxobutanoic acids and undergo cyclization to 3-hydrazono-3*H*-furan-2-one derivatives by the action of acetic anhydride [1, 2]. Neither spontaneous nor thermally induced intramolecular cyclization of 4-R-2-(methylidenehydrazono)-4-oxobutanoic acids into N-substituted 5-aryl-3-hydrazono-3*H*-furan-2-ones was reported in [1, 2], though intramolecular ring closure of structurally related 4-aryl(hetaryl)-2-arylamino-4-oxobut-2-enoic acids into 5-R-3-arylimino-3*H*-furan-2-ones was noted in [3, 4].

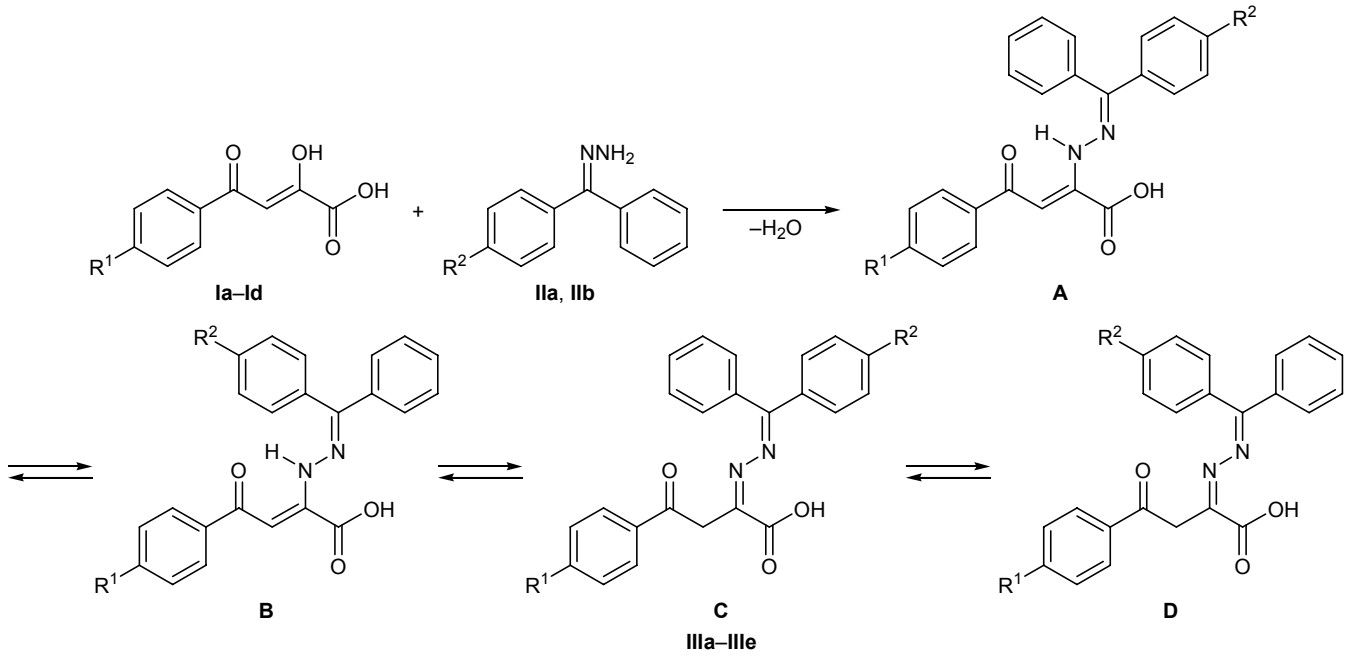
We continued studies in the field of synthesis of N-substituted 4-R-2-hydrazino-4-oxobut-2-enoic acids with a view to examine their tautomeric transformations and intramolecular cyclization. Initially, by reaction of 4-aryl-2-hydroxy-4-oxobut-2-enoic acids **Ia**–**Id** with substituted benzophenone hydrazones **IIa** and **IIb** we obtained (2*Z*)-4-aryl-2-{2-[(*E*)-aryl(phenyl)methylene]hydrazino}-4-oxobut-2-enoic acids **IIIa**–**IIIe** (Scheme 1). Unlike previously reported (2*Z*)-4-aryl-2-[2-(diphenylmethylidene)hydrazino]-4-oxobut-2-enoic acids, molecules **IIIa**–**IIIe** contained a substituent in the *para* position of one aromatic ring. The yields of **IIIa**–**IIIe** were 81–87%.

In the IR spectra of crystalline samples of **IIIa**–**IIIe** (mineral oil) we observed a shoulder at 1599–1602 cm^{-1}, and a broadened absorption band was present in the region 3226–3258 cm^{-1} (νNH), indicating that these compounds exist as enhydrazine tautomer **A** or **B** with the carboxylic group involved in intra- or intermolecular hydrogen bond [2].

According to the ^{1}H NMR data, compounds **IIIa**–**IIIe** in DMSO-d_6 solution give rise to equilibrium tautomeric mixtures of ketoenehydrazine (**A**, **B**) and ketohydrazone structures (**C**, **D**) with *syn* and *anti* orientation of substituents at the N′=C bond. Presumably, the existence of tautomeric equilibrium in a polar solvent is related to stabilization of ketohydrazone structure due to formation of conjugated Ar_2C=N–N=C–C=O bond sequence. Enehydrazine tautomers **A** (*Z*,*E*) and **B** (*Z*,*Z*) are characterized by a singlet from the vinylic proton at δ 6.02–6.14 or 6.09–6.19 ppm and a singlet from the NH proton at δ 12.64–12.76 or

* For communication V, see [1].

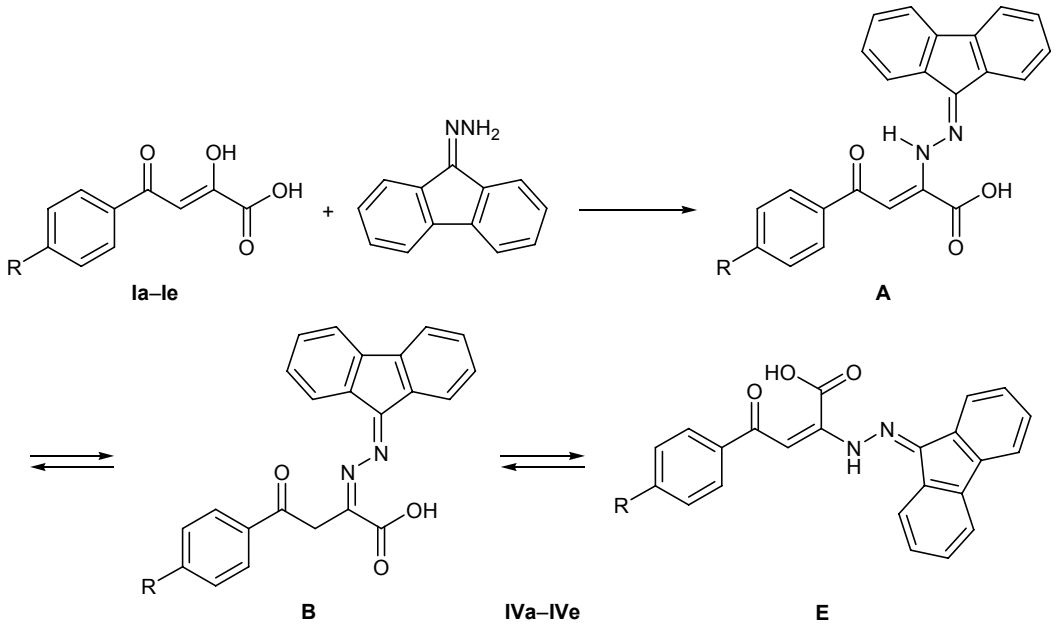
Scheme 1.



I, R^1 = H (**a**), Me (**b**), MeO (**c**), Cl (**d**); **II**, R^2 = Me (**a**), MeO (**b**); **III**, R^1 = MeO, R^2 = Me (**a**); R^1 = H, R^2 = MeO (**b**); R^1 = Me, R^2 = MeO (**c**); R^1 = R^2 = MeO (**d**); R^1 = Cl, R^2 = MeO (**e**).

12.73–12.85 ppm, respectively [5]. The downfield position of the NH signal is determined by intramolecular hydrogen bonding between the NH proton and C^4=O carbonyl oxygen atom. The overall fraction of structures **A** and **B** ranges from 63 to 79%, the former prevailing (35–45%), which is quite consistent with published data [5, 6]. Hydrazone tautomers **C** (*E*) and **D** (*Z*) give rise to a singlet from the C^3H_2 methylene group at δ 4.39–4.54 and 4.45–4.60 ppm, respectively. The equilibrium between structures **C** and **D** is displaced toward the former, presumably for steric and thermodynamic reasons. Unlike 4-aryl-2-[2-(2-oxo-

Scheme 2.



R = H (**a**), Me (**b**), MeO (**c**), Cl (**d**), EtO (**e**).

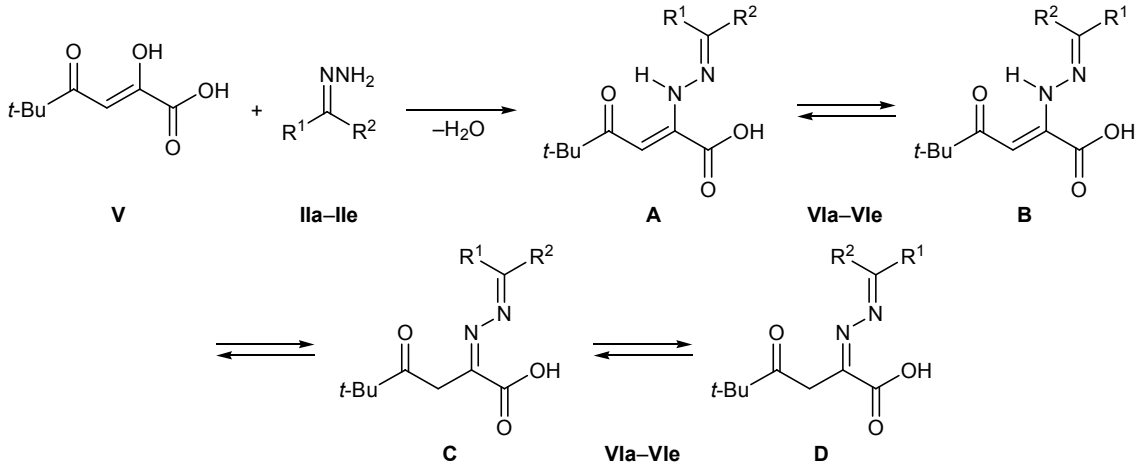
1,2-diphenylethylidene)hydrazino]-4-oxobut-2-enoic acids [1], no ketoenehydrazine tautomers of **IIIa**–**IIIe** with *E* configuration of the double C=C bond were detected in DMSO-d_6 solution, which may be due to additional stabilization of *Z*-isomeric structures **C** and **D** via formation of strong intramolecular hydrogen bond.

Replacement of the aryl(phenyl)methylidene fragment by fluoren-9-ylidene fragment in which both aromatic rings are fixed in one plane does not change the reaction direction. 4-Aryl-2-hydroxy-4-oxobut-2-enoic acids **Ia**–**Ie** reacted with fluorenone hydrazone to give (2*Z*)-4-aryl-2-[2-(9*H*-fluoren-9-ylidene)hydrazino]-4-oxobut-2-enoic acids **IVa**–**IVe** in 81–94% yield (Scheme 2). Compounds **IVa**–**IVe** displayed in the IR spectra (mineral oil) a shoulder at 1564–1568 cm^{-1} and a broadened absorption band in the region 3304–3314 cm^{-1} due to stretching vibrations of the NH group; these findings indicate that acids **IVa**–**IVe** in the crystalline state have enehydrazine structure and that the carboxylic group is involved in intra- or intermolecular hydrogen bond (or the nitrogen atom is protonated by the carboxylic group) [2]. The ^{1}H NMR data allowed us to conclude that, unlike derivatives **IIIa**–**IIIe**, compounds **IVa** and **IVc**–**IVe** in DMSO-d_6 exist as two tautomeric ketoenehydrazine (**A**) and ketohydrazone structures (**C**), the fraction of tautomer **A** being 29–47%. Presumably, structure **C** predominates due to formation of the C=N–N=C–C=O conjugated bond system which is additionally stabilized by the fluorenylidene fragment oriented in the same plane. By contrast, the aryl substituents in benzophenone derivatives **IIIa**–**IIIe** and (2*Z*)-4-aryl-2-[2-(diphenylmethylidene)hydrazino]-4-oxobut-2-enoic acids [2] are most likely to be forced out from conjugation with the C=N–N=C–C=O fragment for steric reasons; as a result, structure **C** prevails due to additional stabilization by intramolecular hydrogen bond C^4=O···HN. Enehydrazine tautomer **A** is characterized by vinylic proton signal at δ 6.51–6.54 ppm and NH singlet at δ 13.78–13.85 ppm. Hydrazone structure **C** gives a two-proton singlet from the C^3H_2 methylene group at δ 4.41–4.48 ppm. Signal from the carboxy proton was not detected, presumably because of its considerable broadening.

The ^{1}H NMR spectra of compounds **IVb** and **IVd** in $CDCl_3$ displayed a different pattern. The spectra lacked signals assignable to ketohydrazone structure **C**, whereas those belonging to *E*-isomeric ketoenehydrazine **E** were observed in addition to signals of *Z*-ketoenehydrazine **A**. This may be rationalized in terms of weaker solvation by less polar $CDCl_3$ which, unlike DMSO-d_6, weakens intramolecular hydrogen bonds thus destabilizing ketoenehydrazine structures **A** and **E**. Tautomer **A** displays the NH signal at δ 14.24 (**IVb**) or 14.26 ppm (**IVd**); the corresponding signal of *E*-isomeric ketoenehydrazine **E** is observed at δ 10.88 (**IVb**) or 10.95 ppm (**IVd**). The vinylic 3-H proton signal of both **A** and **E** is overlapped by aromatic proton signals. The downfield position of that signal may result from formation of strong intramolecular hydrogen bond and additional effect of the fluorenylidene substituent through the *p*–π conjugation system involving nitrogen atoms [7]. No carboxy proton signal was observed in the ^{1}H NMR spectra of these compounds.

We also examined reactions of 2-hydroxy-5,5-dimethyl-4-oxohex-2-enoic acid (**V**) with hydrazones derived from substituted benzophenones and fluorenone. In all cases, the corresponding 5,5-dimethyl-2-

Scheme 3.



R^1 = Ph, R^2 = 4-MeC_6H_4 (**a**), 4-$MeOC_6H_4$ (**b**), 4-BrC_6H_4 (**c**), Ph (**d**); R^1R^2 = biphenyl-2,2′-diyl (**e**).

(2-ylidenehydrazino)-4-oxohex-2-enoic acids **VIa**–**VIe** were obtained in 45–86% yield (Scheme 3), i.e., replacement of the 4-aryl substituent in acids **I** by *tert*-butyl group did not result in change of the reaction direction. The IR spectra of crystalline compounds **VIa**–**VIe** (mineral oil) contained a broadened absorption band at 3304–3314 cm^{-1} (NH), absorption bands due to carboxylic (1723–1745 cm^{-1}) and carbonyl groups (C^4=O, 1598–1603 cm^{-1}), and an absorption band in the region 1576–1582 cm^{-1}, which is typical of stretching vibrations of C=C and C=N bonds. Broadening of the NH band and low-frequency position of the C^4=O band suggest that acids **VIa**–**VIe** in the crystalline state exist as enehydrazine tautomers stabilized by intramolecular hydrogen bond C^4=O···HN [2, 8]. The ^{1}H NMR spectra of **VIa**–**VIe** in DMSO-d_6 considerably differed from each other. The spectra of **IVa**–**IVc** were consistent with the existence of these compounds in solution as two *Z*-isomeric ketoenehydrazine tautomers **A** and **B** and two ketohydrazone tautomers **C** and **D**, structure **A** prevailing (cf. the above data for acids **IIIa**–**IIId**). Enehydrazines **A** (*Z*,*E*) and **B** (*Z*,*Z*) are characterized by the position of vinylic proton singlet at δ 5.36–5.40 and 5.42–5.49 ppm and of NH singlet at δ 11.92–12.13 and 12.01–12.16 ppm, respectively. The NH signal is displaced downfield as a result of intramolecular hydrogen bonding with the C^4=O carbonyl oxygen atom. The fraction of structure **A** is 31–36%, and the fraction of **B** is 20–23%. Hydrazones **C** (*E*) and **D** (*Z*) each displayed a singlet from the C^3H_2 methylene protons at δ 3.94–3.98 and 3.98–4.0 ppm, respectively. The fraction of **C** is 27–30%, and the fraction of **D** is 14–19%.

A different pattern is observed in the ^{1}H NMR spectra of compounds **VId** and **VIe**. Apart from signals belonging to the *Z* isomer (structure **A**, 80 and 16%, respectively; δ_{NH} 12.11 and 13.32 ppm, $\delta_{3\text{-}H}$ 5.5 and 5.92 ppm), the spectra contained signals assignable to β-ketohydrazone tautomer **C**, δ 3.98 and 4.01 ppm (C^3H_2), respectively. No isomer with *E* configuration of the C^2=C^3 bond was detected in the ^{1}H NMR spectra of compounds **VIa**–**VIe**.

EXPERIMENTAL

The IR spectra were measured on an FSM-1201 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were recorded on Bruker DRX-500 (500.13 MHz) and Varian Mercury Plus-300 instruments (300.05 MHz) using DMSO-d_6 as solvent and hexamethyldisiloxane as internal reference. The purity of the isolated compounds was checked, and the progress of reactions was monitored, by TLC on Silufol UV-254 plates using diethyl ether–benzene–acetone (10:9:1) as eluent; spots were detected by treatment with iodine vapor.

4-Aryl-2-{2-[aryl(phenyl)methylidene]hydrazino}-4-oxobut-2-enoic acids IIIa–IIIe (*general procedure*). A solution of 0.001 mol of hydrazone **IIa** or **IIb** in 20 ml of chloroform was added to a solution of 0.01 mol of 4-aryl-2-hydroxy-4-oxobut-2-enoic acid **Ia**–**Id** in 20 ml of ethanol. The mixture was kept for 24 h at 20–25°C and cooled to 0°C, and the precipitate was filtered off and recrystallized from appropriate solvent.

2-{2-[(4-Methoxyphenyl)(phenyl)methylidene]-hydrazino}-4-oxo-4-phenylbut-2-enoic acid (IIIa). Yield 3.41 g (88%), orange crystals, mp 165–167°C (from EtOH–$CHCl_3$). IR spectrum, ν, cm^{-1}: 3226 br (NH), 1602 sh (COO, C=O, C=N). ^{1}H NMR spectrum, δ, ppm: **A** (43.5%): 3.83 s (3H, OMe), 6.12 s (1H, CH), 7.65 m (14H, H_{arom}), 12.75 s (1H, NH); **B** (35.5%): 3.95 s (3H, OMe), 6.18 s (1H, CH), 7.65 m (14H, H_{arom}), 12.84 s (1H, NH); **C** (15%); 3.88 s (3H, OMe), 4.49 s (2H, CH_2), 7.65 m (14H, H_{arom}); **D** (6%): 3.91 s (3H, OMe), 4.58 s (2H, CH_2), 7.65 m (14H, H_{arom}). Found, %: C 71.40; H 4.94; N 7.22. $C_{23}H_{19}N_2O_4$. Calculated, %: C 71.31; H 4.94; N 7.23.

4-(4-Methoxyphenyl)-2-{2-[(4-methoxyphenyl)-(phenyl)methylidene]hydrazino}-4-oxobut-2-enoic acid (IIIb). Yield 3.53 g (82%), orange crystals, mp 182–183°C (from EtOH–$CHCl_3$). IR spectrum, ν, cm^{-1}: 3257 br (NH), 1605 sh (COO, C=O, C=N). ^{1}H NMR spectrum, δ, ppm: **A** (45%): 3.80 s (3H, OMe), 3.83 s (3H, OMe), 6.09 s (1H, CH), 7.65 m (13H, H_{arom}), 12.64 s (1H, NH); **B** (30%): 3.78 s (3H, OMe), 3.90 s (3H, OMe), 6.04 s (1H, CH), 7.65 m (13H, H_{arom}), 12.64 s (1H, NH); **C** (23%): 3.81 s (3H, OMe), 3.86 s (3H, OMe), 4.39 s (2H, CH_2), 7.65 m (13H, H_{arom}); **D** (2%): 3.77 s (3H, OMe), 3.88 s (3H, OMe), 4.45 s (2H, CH_2), 7.65 m (13H, H_{arom}). Found, %: C 69.72; H 5.16; N 6.52. $C_{25}H_{22}N_2O_5$. Calculated, %: C 69.76; H 5.15; N 6.51.

2-{2-[(4-Methoxyphenyl)(phenyl)methylidene]-hydrazino}-4-(4-methylphenyl)-4-oxobut-2-enoic acid (IIIc). Yield 3.36 g (81%), orange crystals, mp 157–158°C (from EtOH–$CHCl_3$). IR spectrum, ν, cm^{-1}: 3251 br (NH), 1599 sh (COO, C=O, C=N). ^{1}H NMR spectrum, δ, ppm: **A** (45%): 2.38 s (3H, Me), 3.82 s (3H, OMe), 6.02 s (1H, CH), 7.65 m (13H, H_{arom}), 12.73 s (1H, NH); **B** (30%): 2.37 s (3H, Me),

3.94 s (3H, OMe), 6.14 s (1H, CH), 7.65 m (13H, H_{arom}), 12.82 s (1H, NH); **C** (23%): 2.41 s (3H, Me), 3.87 s (3H, OMe), 4.54 s (2H, CH_2), 7.65 m (13H, H_{arom}); **D** (2%): 2.40 s (3H, Me), 3.90 s (3H, OMe), 4.52 s (2H, CH_2), 7.65 m (13H, H_{arom}). Found, %: C 72.42; H 5.36; N 6.72. $C_{25}H_{22}N_2O_5$. Calculated, %: C 72.45; H 5.35; N 6.76.

4-(4-Chlorophenyl)-2-{2-[(4-methoxyphenyl)-(phenyl)methylidene]hydrazino}-4-oxobut-2-enoic acid (IIId). Yield 3.76 g (87%), orange crystals, mp 134–135°C (from EtOH–$CHCl_3$). IR spectrum, ν, cm^{-1}: 3258 br (NH), 1605 sh (COO, C=O, C=N). ^1H NMR spectrum, δ, ppm: **A** (35%): 3.83 s (3H, OMe), 6.14 s (1H, CH), 7.65 m (13H, H_{arom}), 12.76 s (1H, NH); **B** (28%): 3.95 s (3H, OMe), 6.19 s (1H, CH), 7.65 m (13H, H_{arom}), 12.82 s (1H, NH); **C** (20%): 3.85 s (3H, OMe), 4.47 s (2H, CH_2), 7.65 m (13H, H_{arom}); **D** (17%): 3.91 s (3H, OMe), 4.60 s (2H, CH_2), 7.65 m (13H, H_{arom}). Found, %: C 72.27; H 4.36; Cl 8.18; N 6.42. $C_{24}H_{19}ClN_2O_4$. Calculated, %: C 66.29; H 4.40; Cl 8.15; N 6.44.

4-(4-Methoxyphenyl)-2-{2-[(4-methylphenyl)-(phenyl)methylidene]hydrazino}-4-oxobut-2-enoic acid (IIIe). Yield 2.9 g (88%), orange crystals, mp 151–152°C (from toluene). IR spectrum, ν, cm^{-1}: 3237 br (NH), 1604 sh (COO, C=O, C=N). ^1H NMR spectrum, δ, ppm: **A** (36%): 2.36 s (3H, Me), 3.84 s (3H, OMe), 6.12 s (1H, CH), 7.65 m (13H, H_{arom}), 12.69 s (1H, NH); **B** (35%): 2.52 s (3H, Me), 3.91 s (3H, OMe), 6.15 s (1H, CH), 7.65 m (13H, H_{arom}), 12.73 s (1H, NH); **C** (25%): 2.32 s (3H, Me), 3.87 s (3H, OMe), 4.43 s (2H, CH_2), 7.65 m (13H, H_{arom}); **D** (4%): 2.42 s (3H, Me), 3.89 s (3H, OMe), 4.52 s (2H, CH_2), 7.65 m (13H, H_{arom}). Found, %: C 72.43; H 5.35; N 6.74. $C_{25}H_{22}N_2O_5$. Calculated, %: C 72.45; H 5.35; N 6.76.

4-Aryl-2-[2-(9*H*-fluoren-9-ylidene)hydrazino]-4-oxobut-2-enoic acids IVa–IVe (*general procedure*). A solution of 0.01 mol of fluorenone hydrazone in 20 ml of ethanol was added to a solution of 0.01 mol of 4-aryl-2-hydroxy-4-oxobut-2-enoic acid **Ia**–**Ie** in 20 ml of ethanol, and the mixture was kept for 24 h at 20–25°C. The mixture was cooled to 0°C, and the precipitate was filtered off and recrystallized from toluene.

2-[2-(9*H*-Fluoren-9-ylidene)hydrazino]-4-oxo-4-phenylbut-2-enoic acid (IVa). Yield 3.46 g (94%), red crystals, mp 190–190.5°C (from toluene). IR spectrum, ν, cm^{-1}: 3314 br (NH), 1568 sh (COO, C=O, C=N). ^1H NMR spectrum, δ, ppm: **A** (32%): 6.54 s (1H, CH), 7.70 m (13H, H_{arom}), 13.85 s (1H, NH); **C** (68%): 4.48 s (2H, CH_2), 7.70 m (13H, H_{arom}). Found, %: C 75.03; H 4.41; N 7.58. $C_{23}H_{16}N_2O_3$. Calculated, %: C 74.99; H 4.38; N 7.60.

2-[2-(9*H*-Fluoren-9-ylidene)hydrazino]-4-(4-methylphenyl)-4-oxobut-2-enoic acid (IVb). Yield 3.1 g (81%), red crystals, mp 187–188°C (from $CHCl_3$). IR spectrum, ν, cm^{-1}: 3304 br (NH), 1566 sh (COO, C=O, C=N). ^1H NMR spectrum, δ, ppm ($CDCl_3$): **A** (18%): 2.44 s (3H, Me), 7.60 s (13H, H_{arom}), 14.38 s (1H, NH); **E** (82%): 2.48 s (3H, Me), 7.60 s (13H, H_{arom}), 10.88 s (1H, NH). Found, %: C 75.26; H 4.75; N 7.31. $C_{24}H_{18}N_2O_3$. Calculated, %: C 75.38; H 4.74; N 7.33.

2-[2-(9*H*-Fluoren-9-ylidene)hydrazino]-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid (IVc). Yield 3.86 g (94%), red crystals, mp 194–195°C (from toluene). IR spectrum, ν, cm^{-1}: 3312 br (NH), 1568 sh (COO, C=O, C=N). ^1H NMR spectrum, δ, ppm: **A** (29%): 3.87 s (3H, OMe), 6.51 s (1H, CH), 7.60 m (12H, H_{arom}), 13.84 s (1H, NH); **C** (68 %): 3.81 s (3H, OMe), 4.42 s (2H, CH_2), 7.60 m (12H, H_{arom}). Found, %: C 71.60; H 4.56; N 7.05. $C_{23}H_{18}N_2O_4$. Calculated, %: C 71.56; H 4.55; N 7.03.

4-(4-Chlorophenyl)-2-[2-(9*H*-fluoren-9-ylidene)-hydrazino]-4-oxobut-2-enoic acid (IVd). Yield 3.62 g (90%), red crystals, mp 172–173°C (from toluene). IR spectrum, ν, cm^{-1}: 3302 br (NH), 1564 sh (COO, C=O, C=N). ^1H NMR spectrum, δ, ppm: **A** (47%): 6.52 s (1H, CH), 7.6 m (12H, H_{arom}), 13.78 s (1H, NH); **C** (53%): 4.43 s (2H, CH_2), 7.60 m (12H, H_{arom}). ^1H NMR spectrum in $CDCl_3$, δ, ppm: **A** (55%): 7.60 s (13H, CH, H_{arom}), 14.26 s (1H, NH); **E** (45%): 7.60 s (13H, CH, H_{arom}), 10.895 s (1H, NH). Found, %: C 68.55; H 3.76; Cl 8.84; N 6.94. $C_{23}H_{15}ClN_2O_3$. Calculated, %: C 68.58; H 3.75; Cl 8.80; N 6.95.

4-(4-Ethoxyphenyl)-2-[2-(9*H*-fluoren-9-ylidene)-hydrazino]-4-oxobut-2-enoic acid (IVe). Yield 3.79 g (92%), red crystals, mp 201–202°C (from toluene). IR spectrum, ν, cm^{-1}: 3308 br (NH), 1566 sh (COO, C=O, C=N). ^1H NMR spectrum, δ, ppm: **A** (36%): 1.36 t (3H, Me), 4.14 q (3H, OCH_2), 6.51 s (1H, CH), 7.60 m (12H, H_{arom}), 13.85 s (1H, NH); **C** (64%): 1.32 t (3H, Me), 4.08 q (3H, OCH_2), 4.41 s (2H, CH_2), 7.60 m (12H, H_{arom}). Found, %: C 72.82; H 4.86; N 6.74. $C_{25}H_{20}N_2O_4$. Calculated, %: C 72.80; H 4.89; N 6.79.

2-{2-[Aryl(phenyl)methylidene]hydrazino}-5,5-dimethyl-4-oxohex-2-enoic acids VIa–VId and 2-[2-(9*H*-fluoren-9-ylidene)hydrazino]-5,5-dimethyl-4-oxohex-2-enoic acid (VIe) (*general procedure*).

A solution of 0.01 mol of hydrazone **IIa–IIe** in 20 ml of ethanol or toluene was added to a solution of 1.72 g (0.01 mol) of 2-hydroxy-5,5-dimethyl-4-oxohex-2-enoic acid (**V**) in 15 ml of ethanol. The mixture was heated for 3–4 min and kept for 24 h at 20–25°C, and the precipitate was filtered off and recrystallized from toluene or ethanol.

2-[2-(Diphenylmethylidene)hydrazino]-5,5-dimethyl-4-oxohex-2-enoic acid (VIa). Yield 3.01 g (86%), yellow crystals, mp 151–152°C (from ethanol). IR spectrum, ν, cm^{-1}: 1744 (COOH); 1597, 1577 (C=C, C=O, C=N). ^{1}H NMR spectrum, δ, ppm: **A** (80%): 0.99 s (9H, CMe_3) 5.50 s (1H, CH), 7.50 m (10H, H_{arom}), 12.11 s (1H, NH), 13.97 br.s (1H, COOH); **C** (20%): 1.05 s (9H, CMe_3) 3.98 s (2H, CH_2), 7.50 m (10H, H_{arom}), 13.97 br.s (1H, COOH). Found, %: C 71.95; H 6.28; N 7.94. $C_{21}H_{22}N_2O_3$. Calculated, %: C 71.98; H 6.33; N 7.99.

5,5-Dimethyl-2-{2-[(4-methylphenyl)(phenyl)methylidene]hydrazino}-4-oxohex-2-enoic acid (VIb). Yield 2.73 g (75%), orange crystals, mp 136–137°C (from ethanol). IR spectrum, ν, cm^{-1}: 1743 (COOH); 1603, 1582 (C=C, C=O, C=N). ^{1}H NMR spectrum, δ, ppm: **A** (31%): 1.02 s (9H, CMe_3), 2.37 s (3H, Me), 5.37 s (1H, CH), 7.40 m (9H, H_{arom}), 11.92 s (1H, NH); **B** (20%): 1.14 s (9H, CMe_3), 2.35 s (3H, Me), 5.43 s (1H, CH), 7.40 m (9H, H_{arom}), 12.03 s (1H, NH); **C** (30%): 0.98 s (9H, CMe_3), 2.33 s (3H, Me), 3.95 s (2H, CH_2), 7.40 m (9H, H_{arom}); **D** (19%): 1.06 s (9H, CMe_3), 2.43 s (3H, Me), 3.99 s (2H, CH_2), 7.40 m (9H, H_{arom}). Found, %: C 72.51; H 6.62; N 7.68. $C_{22}H_{24}N_2O_3$. Calculated, %: C 72.50; H 6.64; N 7.69.

2-{2-[(4-Methoxyphenyl)(phenyl)methylidene]-hydrazino}-5,5-dimethyl-4-oxohex-2-enoic acid (VIc). Yield 1.71 g (45%), orange crystals, mp 152–153°C (from ethanol). IR spectrum, ν, cm^{-1}: 3257 (NH); 1749 (COOH); 1603, 1571 (C=C, C=O, C=N). ^{1}H NMR spectrum, δ, ppm: **A** (30%): 0.99 s (9H, CMe_3), 3.71 s (3H, OMe), 5.36 s (1H, CH), 7.40 m (9H, H_{arom}), 11.92 s (1H, NH); **B** (20%): 1.12 s (9H, CMe_3), 3.75 s (3H, OMe), 5.42 s (1H, CH), 7.40 m (9H, H_{arom}), 12.01 s (1H, NH); **C** (30%): 0.97 s (9H, CMe_3), 3.83 s (3H, OMe), 3.94 s (2H, CH_2), 7.40 m (9H, H_{arom}); **D** (20%): 1.05 s (9H, CMe_3), 3.92 s (3H, OMe), 3.98 s (2H, CH_2), 7.40 m (9H, H_{arom}). Found, %: C 69.43; H 6.32; N 7.38. $C_{22}H_{24}N_2O_4$. Calculated, %: C 69.46; H 6.36; N 7.36.

2-{2-[(4-Bromophenyl)(phenyl)methylidene]hydrazino}-5,5-dimethyl-4-oxohex-2-enoic acid (VId). Yield 1.71 g (59%), orange crystals, mp 150–151°C (from toluene). IR spectrum, ν, cm^{-1}: 1745 (COOH); 1598, 1577 (C=C, C=O, C=N). ^{1}H NMR spectrum, δ, ppm: **A** (36%): 0.98 s (9H, CMe_3), 5.36 s (1H, CH), 7.50 m (9H, H_{arom}), 12.13 s (1H, NH); **B** (23%): 1.04 s (9H, CMe_3), 5.49 s (1H, CH), 7.50 m (9H, H_{arom}), 12.16 s (1H, NH); **C** (27%): 1.0 s (9H, CMe_3), 3.98 s (2H, CH_2), 7.40 m (9H, H_{arom}); **D** (14%): 1.05 s (9H, CMe_3), 4.0 s (2H, CH_2), 7.40 m (9H, H_{arom}). Found, %: C 58.73; H 4.91; Br 18.65; N 6.51. $C_{21}H_{21}BrN_2O_3$. Calculated, %: C 58.75; H 4.93; Br 18.61; N 6.53.

2-[2-(9*H*-Fluoren-9-ylidene)hydrazino]-5,5-dimethyl-4-oxohex-2-enoic acid (VIe). Yield 2.54 g (73%), orange crystals, mp 174–175°C (from toluene). IR spectrum, ν, cm^{-1}: 3318 (NH); 1723 (COOH); 1602, 1576 (C=C, C=O, C=N). ^{1}H NMR spectrum, δ, ppm: **A** (16%): 1.19 s (9H, CMe_3), 5.92 s (1H, CH), 7.70 m (9H, H_{arom}), 13.32 s (1H, NH), 13.50 br.s (COOH); **C** (86%): 1.02 s (9H, CMe_3), 4.01 s (2H, CH_2), 7.70 m (4H, H_{arom}), 13.50 br.s (COOH). Found, %: C 72.43; H 5.81; N 8.01. $C_{21}H_{20}N_2O_3$. Calculated, %: C 72.40; H 5.79; N 8.04.

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