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# Synthesis of the *E* and *Z* Isomers of 3-(5-Aryl-1,3,4-oxadiazol-2-yl)acrylic Acids

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**Abstract**—Two procedures have been proposed for the synthesis of pure (*E*)- and (*Z*)-3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids, by one-step cyclization of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids or via initial cyclization of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids to 5-(aroylhydrazinylidene)furan-2(5*H*)-ones which are then converted into the target compounds.

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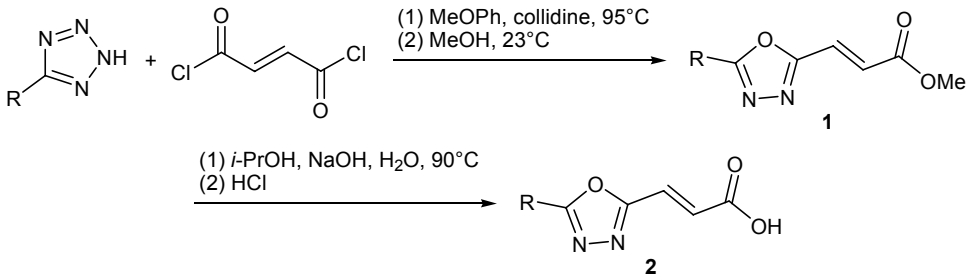
Many 1,3,4-oxadiazole derivatives possessing a conjugated bond system exhibit luminescence and semiconducting properties and are used as optical bleaching agents, fluorescent dyes [1], and components of active media for liquid lasers [2]. Organic light-emitting diodes [3–6] and electrically conducting materials [7] have been obtained on the basis of thin films prepared from polymers containing 1,3,4-oxadiazole fragments.

The present work was aimed at finding out whether the cyclization of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids can be used for the preparation of isomerically pure (*E*)- and (*Z*)-3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids. Two synthetic approaches to 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids are known. The first of these is based on the reaction of substituted 5-aryltetrazoles with fumaryl chloride [8], which affords methyl 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylates **1**, and hydrolysis of the latter yields the corresponding (*E*)-3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids **2** (Scheme 1). It should be noted that attempts of the same authors [8] to react 5-aryltetrazoles with maleic anhydride with the goal of obtaining (*Z*)-3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids were unsuccessful.

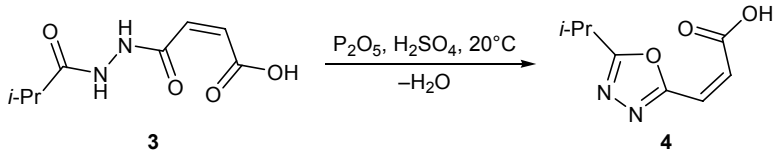
The second approach implies cyclization of 1,2-diacylhydrazines, which can be accomplished in one or two steps. Only a few examples of such syntheses have been reported. In particular, one-step cyclization of (*Z*)-4-(2-isobutyrylhydrazinyl)-4-oxobut-2-enoic acid (**3**) gave (*Z*)-3-(5-isopropyl-1,3,4-oxadiazol-2-yl)-acrylic acid (**4**) (Scheme 2) [9]. The two-step version includes cyclization of 1,2-diacylhydrazines to 5-(acylhydrazinylidene)furan-2(5*H*)-ones (isomaleimides) or maleimides and their subsequent recyclization to 3-(1,3,4-oxadiazol-2-yl)acrylic acids. (*E*)-3-(5-Methyl-1,3,4-oxadiazol-2-yl)acrylic acid [10] and (*E*)-3-[5-(4-ethoxycarbonylphenyl)-1,3,4-oxadiazol-2-yl]acrylic acid [11] were obtained in this way. The latter approach has been poorly explored. We tried to synthesize 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids

**Scheme 1.**




R = 4-$MeOC_6H_4$, 2,5-$Me_2C_6H_3$.

**Scheme 2.**




**3** **4**

by cyclization of the corresponding 1,2-diacylhydrazines, (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids **5**.

Initial acids **5** were prepared in 92–97% yield by acylation of substituted benzoic acid hydrazides with maleic anhydride in glacial acetic acid at room temperature (Scheme 3). Compounds **5** can also be synthesized in high yield using ethyl acetate or diethyl ether as solvent [12]. (*Z*)-4-(2-Aroylhydrazinyl)-4-oxobut-2-enoic acids **5** were subjected to cyclization by the action of phosphoryl chloride in DMF. The complete conversion of **5** was attained in 20–60 min at room temperature. In all cases, the products were mixtures of *E* (**6**) and *Z* isomers (**7**) of 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids, the *E* isomer prevailing. We succeeded by separating isomers **6** and **7** due to their different solubilities in water.

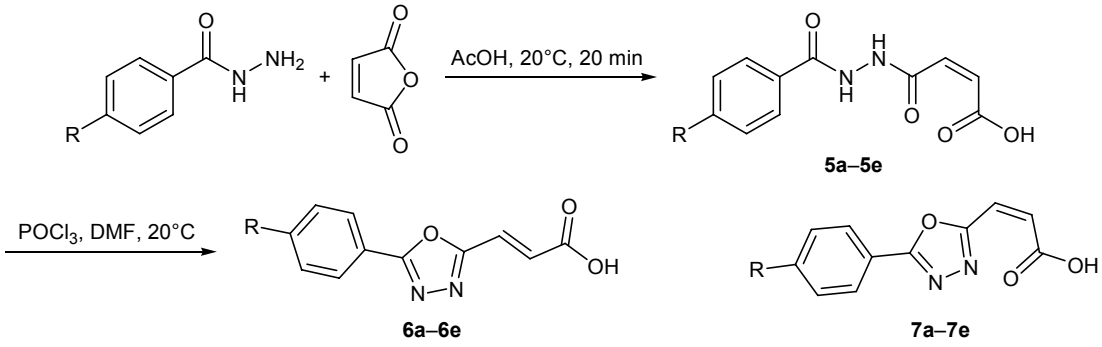
The isomer ratio **6**/**7** strongly depended on the reaction time. As expected, longer reaction time favored formation of the *E* isomer. Our attempts to increase the yield of isomers **7a**–**7c** by shortening the reaction time to several minutes were unsuccessful; they resulted in incomplete conversion of the substrates.

The cyclization of chloro- and nitro-substituted (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids **5d** and **5e** in 20–60 min produced mixtures of (*E*)- and (*Z*)-3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids and the corresponding 5-(aroylhydrazinylidene)furan-2(5*H*)-ones, while the overall fraction of both isomeric acids in the product mixture did not exceed 20%. Longer reaction time led to reduction of the yield of **6** and **7**. Thus, the one-step cyclization of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids by the action of phosphoryl chloride turned out to be inefficient for the synthesis of chloro- and nitro-substituted (*E*)- and (*Z*)-3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids.

The structure of isomeric acids **6** and **7** was confirmed by $^1$H NMR. (*E*)-3-(5-Aryl-1,3,4-oxadiazol-2-yl)acrylic acids **6** are characterized by a larger difference in the chemical shifts of protons on the C=C double bond and a larger spin–spin coupling constant ($J_{trans}$ = 16 Hz against $J_{cis}$ = 12 Hz for *Z* isomers **7**), which is consistent with published data [13]. Furthermore, the $^1$H NOESY spectrum of (*Z*)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)acrylic acid (**7a**) displayed strong cross peaks between the HC=CH protons. The corresponding cross peaks in the NOESY spectrum of *E* isomer **6a** were less intense due to the larger distance between those protons.

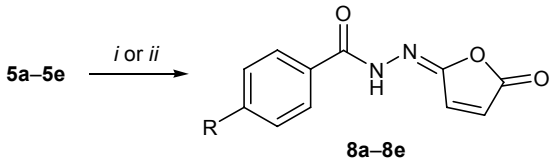
Assuming that the rate of Z–E isomerization of 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids should decrease on lowering the temperature, we carried out the cyclization of acids **5** at lower temperature with a view to increasing the yield of the *Z* isomers. However, the reaction of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids **5** with $POCl_3$ in DMF at 0–10°C afforded only 5-(aroylhydrazinylidene)furan-2(5*H*)-ones **8** in 58–90% yield (Scheme 4). Raising the temperature above 10°C or increasing the reaction time to more than 1 h resulted in the formation of a small amount of (*Z*)-3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids **7**, but the yield of **8** was not improved. We also

**Scheme 3.**




R = H (**a**), Me (**b**), MeO (**c**), Cl (**d**), $O_2N$ (**e**).

**Scheme 4.**

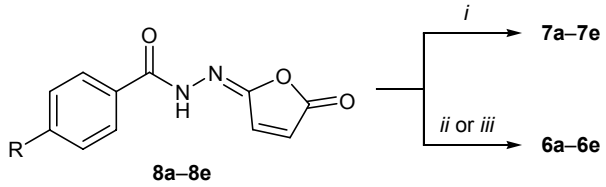



*i*: DMF, $POCl_3$, 0–10°C, 20–60 min; *ii*: $Me_2CO$, EtOCOCl, 30 min, 20°C; R = H (**a**), Me (**b**), MeO (**c**), Cl (**d**), $O_2N$ (**e**).

tried ethyl chloroformate in the presence of triethylamine to cyclize acids **5**. The reactions were carried out at room temperature (30 min), and the products were furanones **8a**–**8e** (yield 54–81%).

Presumably, the cyclization of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids **5** initially gives furanones **8** which then undergo recyclization to 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids. For instance, 5-(acetylhydrazinylidene)furan-2(5*H*)-one was reported to rearrange into (*E*)-3-(5-methyl-1,3,4-oxadiazol-2-yl)acrylic acid on heating in boiling acetic acid [10]. In fact, by heating compounds **8a**–**8e** in boiling acetic acid we obtained (*E*)-3-(5-aryl-1,3,4-oxadiazol-2-yl)-acrylic acids **6a**–**6e**, whereas *Z* isomers **7a**–**7e** were formed in boiling toluene (Scheme 5). By $^1$H NMR monitoring of the transformation of furanones **8** in boiling acetic acid we found that mixtures of *Z* and *E* isomers **6** and **7** were formed at incomplete conversion. After subsequent heating we succeeded in isolating only pure *E* isomers **6a**–**6e** in 55–57% yield. The yields of **6a**–**6e** were improved to 75–92% when the reaction was carried out at room temperature in methylene chloride with addition of acetyl chloride. The yields of **7a**–**7e** in the recyclization in toluene were 64–82%.

**Scheme 5.**




*i*: PhMe, reflux, 1.5 h; *ii*: AcOH, reflux, 4 h; *iii*: AcCl, $CH_2Cl_2$, 24 h, 20°C.

This procedure allowed us to obtain in high yields both *Z* (**7**) and *E* isomers (**6**) of 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids, including chloro- and nitro-substituted derivatives, with high purity, which cannot be achieved by direct cyclization of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids **5**.

In summary, we have developed two procedures for the synthesis of pure *E* and *Z* isomers of 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acid. The first procedure is based on the cyclization of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids by the action of phosphoryl chloride in DMF at room temperature and subsequent separation of isomer mixture by fractional crystallization. The second procedure is more general; it includes recyclization of 5-(aroylhydrazinylidene)-furan-2(5*H*)-ones obtained from (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acids and affords, depending on the conditions, pure *E* or *Z* isomers of 3-(5-aryl-1,3,4-oxadiazol-2-yl)acrylic acids with high yields.

## EXPERIMENTAL

The $^1$H and $^{13}$C NMR spectra were recorded on Bruker Avance DRX-400 and Bruker AM-300 spectrometers, respectively; the $^1$H NOESY spectra were obtained on a Bruker DRX-500 instrument; DMSO-$d_6$ was used as solvent. The IR spectra were measured on a Perkin Elmer Spectrum RX1 spectrometer with Fourier transform from samples dispersed in mineral oil and placed between NaCl plates. The melting points were determined on an Electrothermal IA 9300 Series melting point apparatus. The high-resolution mass spectra (electrospray ionization) were recorded on a Bruker Daltonics MicrOTOF mass spectrometer (ion source temperature 180°C, eluent acetonitrile).

***(Z)*-4-(2-Aroylhydrazinyl)-4-oxobut-2-enoic acids 5a–5e (*general procedure*).** A solution of 0.1 mol of the corresponding benzoic acid hydrazide in 60 mL of glacial acetic acid was added under vigorous stirring to a solution of 10.8 g (0.11 mol) of maleic anhydride in 30 mL of glacial acetic acid. A solid separated from the mixture immediately after the addition was complete. The mixture was stirred for 20 min, and the precipitate was filtered off and washed on a filter with glacial acetic acid.

**(*Z*)-4-(2-Benzoylhydrazinyl)-4-oxobut-2-enoic acid (5a).** Yield 91%, mp 177–179°C; published data [12]: mp 178–179°C. IR spectrum, ν, $cm^{-1}$: 3210 (NH), 2720 (OH), 1707 (C=O), 1651 (C=O, amide), 1628 (C=C), 1588 (C=$C_{arom}$), 1538 (δN–H), 920 (OH), 714 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 6.35 d (1H, *J* = 12.2 Hz), 6.41 d (1H, *J* = 12.3 Hz), 7.48 t (2H, *J* = 7.5 Hz), 7.56 t (1H, *J* = 7.4 Hz), 7.90 d (2H, *J* = 7.5 Hz), 10.65 s (1H), 10.90 s (1H), 13.20 s (1H).

**(*Z*)-4-[2-(4-Methylbenzoyl)hydrazinyl]-4-oxobut-2-enoic acid (5b).** Yield 96%, mp 177–178°C; pub-

lished data [12]: mp 183–185°C. IR spectrum, ν, $cm^{-1}$: 3215 (NH), 2725, 2607 (OH), 1707 (C=O), 1662 (C=O, amide), 1624 (C=C), 1545 (δN–H), 1597, 1517 ($C=C_{arom}$), 921 (OH), 846 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 2.36 s (3H), 6.34 d (1H, *J* = 12.0 Hz), 6.43 d (1H, *J* = 12.3 Hz), 7.29 d (2H, *J* = 8.1 Hz), 7.79 d (2H, *J* = 8.1 Hz), 10.53 s (1H), 10.58 s (1H), 13.26 s (1H).

**(*Z*)-4-[2-(4-Methoxybenzoyl)hydrazinyl]-4-oxobut-2-enoic acid (5c).** Yield 93%, mp 173–174°C; published data [12]: mp 188–189°C. IR spectrum, ν, $cm^{-1}$: 3320 (NH), 2720 (OH), 1722 (C=O), 1663 (C=O, amide), 1630 (C=C), 1606 ($C=C_{arom}$), 1555 (δN–H), 1265 (C–O), 945 (OH), 838 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 3.82 s (3H), 6.35 d (1H, *J* = 12.6 Hz), 6.42 d (1H, *J* = 12.1 Hz), 7.03 d (2H, *J* = 8.4 Hz), 7.88 d (2H, *J* = 8.4 Hz), 10.45 s (1H), 11.40 s (1H), 13.01 s (1H).

**(*Z*)-4-[2-(4-Chlorobenzoyl)hydrazinyl]-4-oxobut-2-enoic acid (5d).** Yield 92%, mp 175–176°C. IR spectrum, ν, $cm^{-1}$: 3239 (NH), 2721 (OH), 1699 (C=O), 1672 (C=O, amide), 1624 (C=C), 1594, 1508 ($C=C_{arom}$), 1543 (δN–H), 952 (OH), 850 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 6.34 d (1H, *J* = 12.5 Hz), 6.40 d (1H, *J* = 12.4 Hz), 7.55 d (2H, *J* = 8.1 Hz), 7.9 d (2H, *J* = 8.1 Hz), 10.62 s (1H), 11.76 s (1H), 13.11 s (1H).

**(*Z*)-4-[2-(4-Nitrobenzoyl)hydrazinyl]-4-oxobut-2-enoic acid (5e).** Yield 97%, mp 182–183°C; published data [12]: mp 195–196°C. IR spectrum, ν, $cm^{-1}$: 3229 (NH), 2605 (OH), 1710 (C=O), 1679 (C=O, amide), 1635 (C=C), 1568 (δN–H), 1590 ($C=C_{arom}$), 1523, 1346 ($NO_2$), 917 (OH), 837 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 6.32 d (1H, *J* = 12.1 Hz), 6.43 d (1H, *J* = 11.9 Hz), 8.11 d (2H, *J* = 8.2 Hz), 8.35 d (2H, *J* = 8.4 Hz), 10.65 s (1H), 10.97 s (1H), 13.10 s (1H).

**(*E*)- and (*Z*)-3-(5-Aryl-1,3,4-oxadiazol-2-yl)prop-2-enoic acids 6a–6c and 7a–7c (*general procedure*).** Phosphoryl chloride, 1.1 mL (0.012 mol), was slowly added under stirring to a solution of 0.01 mol of acid **5a**–**5c** in 10 mL of DMF, maintaining the temperature below 40°C, and the mixture was kept for 20–120 min (depending on the substrate) at room temperature. The mixture was then poured into an ice–water mixture, and the white precipitate of *E* isomer **6** was filtered off and washed on a filter with water. To remove an impurity of the second isomer (if present), the product was recrystallized from ethanol. The filtrate was kept for 12 h at room temperature, and the precipitate of isomer **7** was filtered off, washed on a filter with water, and (if necessary) recrystallized from ethanol.

**(*E*)-3-(5-Phenyl-1,3,4-oxadiazol-2-yl)prop-2-enoic acid (6a).** Yield 52% (20 min), 64% (60 min), mp 191–193°C. IR spectrum, ν, $cm^{-1}$: 2627, 2541 (OH), 1714 (C=O), 1650 (C=C), 1604 ($C=C_{arom}$), 1520 (C=N), 1262, 1175, 1022 (C–O–C), 964 (*trans*-CH=CH), 927 (OH), 688 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 6.94 d (1H, *J* = 15.9 Hz), 7.47 d (1H, *J* = 16.2 Hz), 7.61 m (3H), 8.09 d (2H, *J* = 8.4 Hz), 13.19 s (1H). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 122.96, 124.26, 127.09, 129.46, 129.55, 132.58, 162.32, 164.55, 165.94. Mass spectrum: *m*/*z* 216.0530 $[M]^+$. $C_{11}H_8N_2O_3$. Calculated: *M* 216.0535.

**(*E*)-3-[5-(4-Methylphenyl)-1,3,4-oxadiazol-2-yl]-prop-2-enoic acid (6b).** Yield 54% (60 min), 61% (90 min); mp 208–211°C. IR spectrum, ν, $cm^{-1}$: 2674, 2570 (OH), 1685 (C=O), 1643 (C=C), 1518 (C=N), 1612, 1516 ($C=C_{arom}$), 1279, 1215, 1093 (C–O–C), 970 (*trans*-CH=CH), 826 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 2.39 s (3H), 6.90 d (1H, *J* = 15.9 Hz), 7.41 d (2H, *J* = 7.6 Hz), 7.42 d (1H, *J* = 16.1 Hz), 7.98 d (2H, *J* = 8.2 Hz), 13.22 s (1H).

**(*E*)-3-[5-(4-Methoxyphenyl)-1,3,4-oxadiazol-2-yl]prop-2-enoic acid (6c).** Yield 44% (60 min), 56% (120 min); mp 237–239°C; published data [8]: mp 164°C (decomp.). IR spectrum, ν, $cm^{-1}$: 2617, 2524 (OH), 1715 (C=O), 1647 (C=C), 1617 ($C=C_{arom}$), 1558 (C=N), 1264, 1231, 1178, 1090 (C–O–C), 986 (*trans*-CH=CH), 926 (OH), 832 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 3.84 s (3H), 6.91 d (1H, *J* = 16.2 Hz), 7.17 d (2H, *J* = 8.1 Hz), 7.44 d (1H, *J* = 16.2 Hz), 8.06 d (2H, *J* = 8.1 Hz), 13.18 s (1H).

**(*Z*)-3-(5-Phenyl-1,3,4-oxadiazol-2-yl)prop-2-enoic acid (7a).** Yield 14% (20 min), yield 3% (60 min), mp 155–158°C. IR spectrum, ν, $cm^{-1}$: 2735, 2517 (OH), 1712 (C=O), 1649 (C=C), 1604, 1513 ($C=C_{arom}$), 1550 (C=N), 1217, 1184, 1022 (C–O–C), 814 (*cis*-CH=CH), 927 (OH), 684 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 6.69 d (1H, *J* = 12.3 Hz), 6.92 d (1H, *J* = 12.3 Hz), 7.63 m (3H), 7.99 d (2H, *J* = 7.9 Hz), 13.38 s (1H).

**(*Z*)-3-[5-(4-Methylphenyl)-1,3,4-oxadiazol-2-yl]-prop-2-enoic acid (7b).** Yield 10% (60 min), mp 186–189°C. IR spectrum, ν, $cm^{-1}$: 2585, 2507 (OH), 1710 (C=O), 1647 (C=C), 1612, 1494 ($C=C_{arom}$), 1553 (C=N), 1273, 1175, 1094 (C–O–C), 814 (*cis*-CH=CH), 927 (OH), 816 (*cis*-CH=CH), 825 ($\delta C–H_{arom}$). $^1H$ NMR spectrum, δ, ppm: 2.39 s (3H), 6.66 d (1H, *J* = 12.2 Hz), 6.88 d (1H, *J* = 12.1 Hz), 7.44 d (2H, *J* =

8.5 Hz), 7.88 d (2H, *J* = 8.3 Hz), 13.23 s (1H). Mass spectrum: *m*/*z* 230.0686 $[M]^+$. $C_{12}H_{10}N_2O_3$. Calculated: *M* 230.0691.

**(*Z*)-3-[5-(4-Methoxyphenyl)-1,3,4-oxadiazol-2-yl]prop-2-enoic acid (7c).** Yield 16% (60 min), mp 190–191°C. IR spectrum, ν, $cm^{-1}$: 2726, 2525 (OH), 1721 (C=O), 1640 (C=C), 1610 (C=$C_{arom}$), 1584 (C=N), 1265, 1217, 1175 (C–O–C), 814 (*cis*-CH=CH), 929 (OH), 836 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 3.84 s (3H), 6.64 d (1H, *J* = 12.5 Hz), 6.87 d (1H, *J* = 12.4 Hz), 7.16 d (2H, *J* = 8.5 Hz), 7.92 d (2H, *J* = 8.5 Hz), 13.21 s (1H).

**5-(Aroylhydrazinylidene)furan-2(5*H*)-ones 8a–8e (*general procedures*).** *a*. A solution of 0.0043 mol of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acid **5a**–**5e** in 5 mL of DMF was cooled on an ice bath, and 0.48 mL (0.0052 mol) of phosphoryl chloride was slowly added at such a rate that the temperature did not exceed 10°C. The mixture was kept for 30 min (20 min for **5a** or 60 min for **5d**) at 0–10°C and poured into an ice–water mixture, and the white precipitate was filtered off and washed with water on a filter.

*b*. Triethylamine, 1.53 mL (0.0111 mol), was added to a suspension of 0.0085 mol of (*Z*)-4-(2-aroylhydrazinyl)-4-oxobut-2-enoic acid **5a**–**5e** in 10 mL of acetone, and the mixture became homogeneous. Ethyl chloroformate, 0.9 mL (0.0094 mol), was then slowly added under vigorous stirring, and the mixture was stirred for 30 min and poured into water. The precipitate was filtered off, and thoroughly washed on a filter with cold water and ethanol. Dimethylformamide can also be used as solvent at the same volume ratio.

**5-(Benzoylhydrazinylidene)furan-2(5*H*)-one (8a).** Yield 58% (*a*), 54% (*b*); mp 130–132°C. IR spectrum, ν, $cm^{-1}$: 3497, 3346 (N–H), 1799 (C=O), 1703 (C=N), 1650 (C=O, amide), 1598 (C=$C_{arom}$), 1524 (δN–H), 1250, 1102 (C–O–C), 708 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 6.90 d (1H, *J* = 5.6 Hz), 7.50 t (2H, *J* = 7.5 Hz), 7.59 t (1H, *J* = 7.5 Hz), 7.87 d (2H, *J* = 8.1 Hz), 7.94 d (1H, *J* = 5.6 Hz), 11.69 s (1H). $^{13}$C NMR spectrum, $\delta_C$, ppm: 125.73, 126.67, 128.26, 128.45, 129.57, 132.07, 132.75, 142.35, 166.25. Mass spectrum: *m*/*z* 216.0530 $[M]^+$. $C_{11}H_8N_2O_3$. Calculated: *M* 216.0535.

**5-[(4-Methylbenzoyl)hydrazinylidene]furan-2(5*H*)-one (8b).** Yield 81% (*a*), 71% (*b*); mp 144–146°C. IR spectrum, ν, $cm^{-1}$: 3357 (N–H), 1789 (C=O), 1670 (C=N), 1654 (C=O, amide), 1608 (C=$C_{arom}$), 1539 (δNH), 1263, 1102 (C–O–C), 820 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 2.37 s (3H), 6.92 d (1H, *J* = 5.7 Hz), 7.30 d (2H, *J* = 8.1 Hz), 7.79 d (2H, *J* = 8.1 Hz), 7.93 d (1H, *J* = 5.6 Hz), 11.59 s (1H). $^{13}$C NMR spectrum, $\delta_C$, ppm: 21.11, 125.60, 126.62, 128.51, 128.82, 129.81, 130.09, 142.28, 142.36, 166.27.

**5-[(4-Methoxybenzoyl)hydrazinylidene]furan-2(5*H*)-one (8c).** Yield 82% (*a*), 70% (*b*); mp 152–155°C. IR spectrum, ν, $cm^{-1}$: 3375 (N–H), 1790 (C=O), 1685 (C=N), 1654 (C=O, amide), 1605, 1492 (C=$C_{arom}$), 1526 (δN–H), 1249, 1177, 1096 (C–O–C), 826 (δC–H). $^1$H NMR spectrum, δ, ppm: 3.83 s (3H), 6.90 d (1H, *J* = 5.6 Hz), 7.02 d (2H, *J* = 8.9 Hz), 7.89 d (2H, *J* = 8.9 Hz), 7.93 d (1H, *J* = 5.6 Hz), 11.51 s (1H). $^{13}$C NMR spectrum, $\delta_C$, ppm: 55.5, 113.58, 115.05, 124.67, 125.44, 128.54, 130.55, 142.37, 162.41, 166.32.

**5-[(4-Chlorobenzoyl)hydrazinylidene]furan-2(5*H*)-one (8d).** Yield 76% (*a*), 67% (*b*); mp 163–165°C. IR spectrum, ν, $cm^{-1}$: 3308 (N–H), 1801 (C=O), 1670 (C=N), 1649 (C=O, amide), 1595 (C=$C_{arom}$), 1527 (δN–H), 1263, 1098 (C–O–C), 824 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 6.93 d (1H, *J* = 5.6 Hz), 7.56 d (2H, *J* = 8.5 Hz), 7.89 d (2H, *J* = 8.1 Hz), 7.94 d (1H, *J* = 5.6 Hz), 11.81 s (1H). $^{13}$C NMR spectrum, $\delta_C$, ppm: 117.07, 125.85, 128.32, 128.39, 129.77, 130.45, 131.98, 142.33, 166.21. Mass spectrum: *m*/*z* 250.0140 $[M]^+$. $C_{11}H_7ClN_2O_3$. Calculated: *M* 250.0145.

**5-[(4-Nitrobenzoyl)hydrazinylidene]furan-2(5*H*)-one (8e).** Yield 90% (*a*), 81% (*b*); mp 180–183°C. IR spectrum, ν, $cm^{-1}$: 3376 (N–H), 1791 (C=O), 1689 (C=N), 1646 (C=O, amide), 1604 (C=$C_{arom}$), 1535 (δN–H), 1527, 1348 ($NO_2$), 1282, 1096 (C–O–C), 822 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 6.96 d (1H, *J* = 5.6 Hz), 7.95 d (1H, *J* = 5.6 Hz), 8.08 d (2H, *J* = 8.8 Hz), 8.32 d (2H, *J* = 8.9 Hz), 12.07 s (1H).

**Recyclization of compounds 8a–8e (*general procedures*).** *a*. Compound **8a**–**8e**, 0.008 mol, was dissolved on heating in 30 mL of toluene, and the solution was heated under reflux until an abundant solid precipitated (~90 min). The mixture was cooled, and the precipitate was filtered off and washed on a filter with toluene. Yield, %: **7a**, 64; **7b**, 73; **7c**, 75.

**(*Z*)-3-[5-(4-Chlorophenyl)-1,3,4-oxadiazol-2-yl]-prop-2-enoic acid (7d).** mp 211–214°C. IR spectrum, ν, $cm^{-1}$: 2652, 2590 (OH), 1708 (C=O), 1645 (C=C), 1580 (C=N), 1604, 1507 (C=$C_{arom}$), 1287, 1178, 1094 (C–O–C), 911 (OH), 819 (*cis*-CH=CH), 833 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 6.68 s (1H, *J* = 12.6 Hz), 6.91 d (1H, *J* = 12.3 Hz), 7.69 d (2H, *J* = 8.4 Hz), 7.95 d (2H, *J* = 8.4 Hz), 13.24 s (1H).

**(*Z*)-3-[5-(4-Nitrophenyl)-1,3,4-oxadiazol-2-yl]-prop-2-enoic acid (7e).** mp 206–208°C. IR spectrum, ν, $cm^{-1}$: 2656 (OH), 1697 (C=O), 1644 (C=C), 1607 ($C=C_{arom}$), 1550 (C=N) 1520, 1351 ($NO_2$), 1278, 1175, 1089 (C–O–C), 820 (*cis*-CH=CH), 933 (OH), 854 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 6.73 d (1H, *J* = 12.5 Hz), 6.97 d (1H, *J* = 12.6 Hz), 8.22 d (2H, *J* = 8.5 Hz), 8.45 d (2H, *J* = 8.4 Hz), 13.24 s (1H). Mass spectrum: *m*/*z* 261.0383 $[M]^+$. $C_{11}H_7N_3O_5$. Calculated: *M* 261.0386.

*b*. Compound **8a**–**8e**, 0.008 mol, was dissolved on heating in 20 mL of glacial acetic acid, and the solution was heated for 4 h under reflux, cooled, and poured into cold water. The precipitate was filtered off, washed on a filter with water and ethanol, and reprecipitated from a sodium carbonate solution. Yield, %: **6a**, 55; **6b**, 67; **6c**, 59; **6d**, 65; **6e**, 64.

*c*. Compound **8a**–**8e**, 0.004 mol, was dissolved in 20 mL of methylene chloride (in some cases, 0.5–1 mL of DMF was added to improve the solubility), 1.42 mL (0.02 mol) of acetyl chloride was added, and the mixture was left to stand for 24 h. The precipitate was filtered off and washed with methylene chloride and ethanol. Yield, %: **6a**, 66; **6b**, 75; **6c**, 74; **6d**, 92; **6e**, 91.

**(*E*)-3-[5-(4-Chlorophenyl)-1,3,4-oxadiazol-2-yl]-prop-2-enoic acid (6d).** mp 252–254°C. IR spectrum, ν, $cm^{-1}$: 2590 (OH), 1710 (C=O), 1642 (C=C), 1546 (C=N), 1600 ($C=C_{arom}$), 1263, 1170, 1083 (C–O–C), 915 (OH), 967 (*trans*-CH=CH), 832 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 6.96 d (1H, *J* = 16.0 Hz), 7.46 d (1H, *J* = 16.0 Hz), 7.71 d (2H, *J* = 8.2 Hz), 8.14 d (2H, *J* = 8.4 Hz), 13.27 s (1H).

**(*E*)-3-[5-(4-Nitrophenyl)-1,3,4-oxadiazol-2-yl]-prop-2-enoic acid (6e).** mp 268–270°C. IR spectrum, ν, $cm^{-1}$: 2670 (OH), 1692 (C=O), 1644 (C=C), 1607 ($C=C_{arom}$), 1527 (C=N), 1542, 1351 ($NO_2$), 1294, 1178, 1111 (C–O–C), 970 (*trans*-CH=CH), 934 (OH), 855 (δC–$H_{arom}$). $^1$H NMR spectrum, δ, ppm: 7.00 d (1H, *J* = 16.0 Hz), 7.48 d (1H, *J* = 15.8 Hz), 8.21 d (2H, *J* = 8.1 Hz), 8.36 d (2H, *J* = 8.2 Hz), 13.20 s (1H).

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