

## Furan derivatives

### CCIV. Synthesis and reactions of 5-(2-nitrophenoxy)-2-furaldehyde

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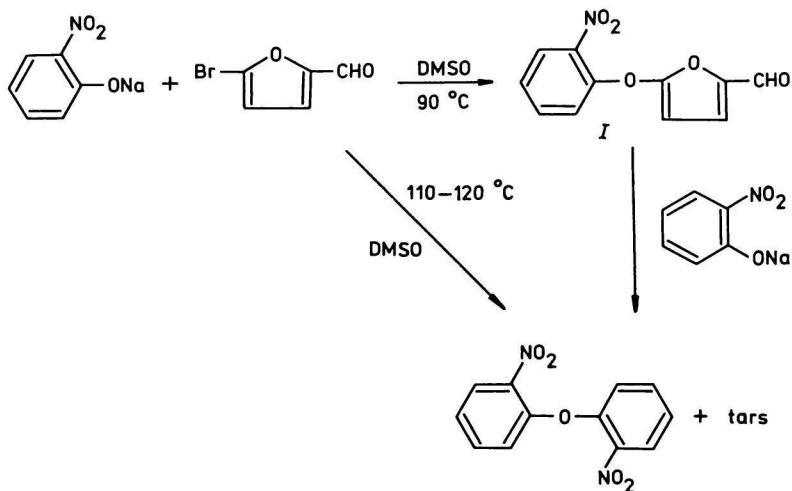
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The preparation and reactions of 5-(2-nitrophenoxy)-2-furaldehyde (*I*) and ethyl 2-(2-nitrophenoxy)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (*VII*) are presented. *I* was prepared by reaction of sodium phenoxide with 5-bromo-2-furaldehyde. Reactions of *I* with malonic acid dinitrile afforded 2-cyano-3-[5-(2-nitrophenoxy)-2-furyl]acrylonitrile and with methyl cyanoacetate methyl 2-cyano-3-[5-(2-nitrophenoxy)-2-furyl] acrylate (*III*) was obtained. *I* with ethyl azidoacetate gave ethyl 2-azido-3-[5-(2-nitrophenoxy)-2-furyl]acrylate which by thermolysis afforded *VII*. Anomalous reaction of *I* with hydroxylammonium chloride in the presence of sodium acetate is described.

В работе описано получение и реакции 5-(2-нитрофенокси)-2-фуральдегида (*I*) и этилового эфира 2-(2-нитрофенокси)-4*H*-фуро[3,2-*b*]пирол-5-карбоксилевой кислоты (*VII*). Соединение *I* было получено реакцией 5-нитрофенолята натрия с 5-бром-2-фуральдегидом. Реакцией *I* с динитрилом малоновой кислоты образуется 2-циано-3-[5-(2-нитрофенокси)-2-фурил]акрилонитрил, с метиловым эфиром циануксусной кислоты был получен метиловый эфир 2-циано-3-[5-(2-нитрофенокси)-2-фурил]акриловой кислоты (*III*). Реакцией *I* с этиловым эфиром азидоуксусной кислоты образуется этиловый эфир 2-азидо-3-[5-(2-нитрофенокси)-2-фурил]акриловой кислоты, из которого термолизом образуется *VII*. Описана аномальная реакция *I* с хлористоводородным гидроксиламином в присутствии ацетата натрия.

In our previous papers we reported the preparation of ethyl 2-(2-nitrophenyl)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylate [1] starting from 5-(2-nitrophenyl)-2-furaldehyde [2] which was used to preparations of pyrrole[2',3':4,5]-furo[3,2-*b*]indole derivatives [3]. This work deals with the synthesis of 5-(2-nitrophenoxy)-2-furaldehyde (*I*) and the study of the influence of oxygen atom between 2-nitrophenoxy and furan rings on the reactivity of this type of compounds. Compound *I* was prepared by the reaction of sodium 2-nitrophenoxide

with 5-bromo-2-furaldehyde in dimethyl sulfoxide at 90 °C. This temperature is optimal, because at 110–120 °C compound *I* is attacked by sodium 2-nitrophenoxide giving 2,2'-dinitrodiphenylether [4] (Scheme 1). The yield of the reaction was increased by bringing down the volume of the solvent. Tanaka and



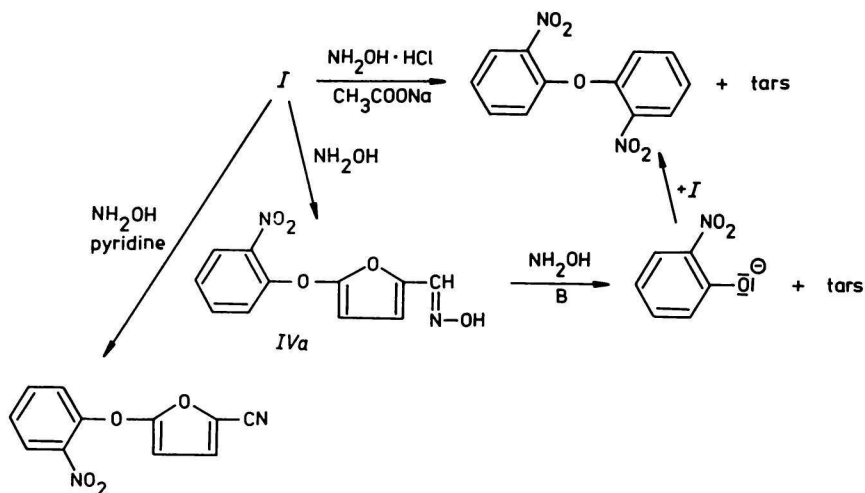
Scheme 1

coworkers [4] prepared *I* by the reaction of potassium 2-nitrophenoxide with 5-nitro-2-furaldehyde at 90 °C. The yield of our procedure was better by more than 20 %.

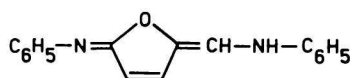
Reactions of *I* with malonic acid dinitrile gave 2-cyano-3-[5-(2-nitrophenoxy)-2-furyl]acrylonitrile (*II*) and with methyl cyanoacetate methyl 2-cyano-3-[5-(2-nitrophenoxy)-2-furyl]acrylate (*III*). Anomalous reaction of *I* with hydroxylammonium chloride in the presence of sodium acetate took place. From the reaction mixture 2,2'-dinitrodiphenylether in 35 % yield was isolated (Scheme 2).

With the aim to study this reaction with similar compounds, we prepared 5-(3-nitrophenoxy)- and 5-(4-nitrophenoxy)-2-furaldehyde [5] and followed them in the reaction with hydroxylammonium chloride under given conditions. We found out that the reaction of these positional isomers of *I* gave the expected corresponding oximes *IVb* and *IVc*. Since by the treatment of *I* with hydroxylammonium chloride in pyridine and acethanhydride at  $\theta = 90$  °C 5-(2-nitrophenoxy)-2-furylcyanide arose (*V*), it seems obvious that the appropriate oxime of *I* is formed primarily. 5-(2-Nitrophenoxy)-2-furaldehydoxime (*IVa*) was obtained by the reaction of *I* with hydroxylamine in pyridine at room temperature.

From the reaction mixture of 5-(2-nitrophenoxy)-2-furaldehydoxime (*IVa*) with sodium 2-nitrophenoxide or 4-nitrophenoxide starting material was isolated after

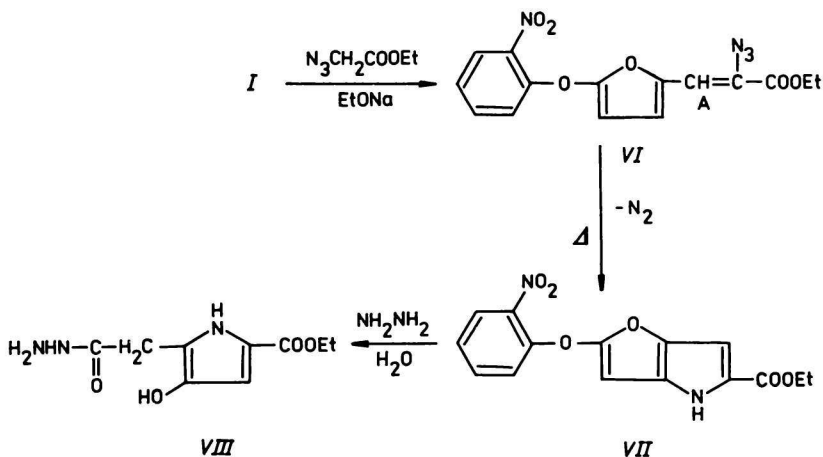


heating during 4 h. From these results it is clear that the precursor of 2,2'-dinitrodiphenylether is not 5-(2-nitrophenoxy)-2-furaldehydoxime but presumably the starting 5-(2-nitrophenoxy)-2-furaldehyde. It was indicated necessary to clarify the formation of 2-nitrophenoxide ion, which by nucleophilic attack on 5-(2-nitrophenoxy)-2-furaldehyde gave 2,2'-dinitrodiphenylether. It is known [6] that 5-bromo-2-furaldehyde with aniline forms in the first step 5-bromo-2-furfurylidene-aniline, which by further nucleophilic substitution with aniline gives unsaturated five-membered ketimine of the following structure [6]



It is possible to assume that 5-(2-nitrophenoxy)-2-furaldehyde reacts with hydroxylamine similarly to give 5-(2-nitrophenoxy)-2-furaldehydoxime (IVa). By further attack of hydroxylamine the nucleophilic reaction takes place giving rise to 2-nitrophenoxide ion, which reacts with I at C-1 phenoxy group and 2,2'-dinitrodiphenylether originates. The formation of 2-nitrophenoxide ion was proved by the reaction of IVa with hydroxylamine (Scheme 2).

By the reaction of I and ethyl azidoacetate in the presence of sodium ethoxide ethyl 2-azido-3-[5-(2-nitrophenoxy)-2-furyl]acrylate (VI) was prepared, which represents thermally and photochemically unstable substituted vinyl azide. Ethyl 2-(2-nitrophenoxy)-4H-furo[3,2-b]pyrrole-5-carboxylate (VII) was formed by thermolysis of VI in boiling toluene (Scheme 3).



Scheme 3

Compound **VII** reacted with hydrazine in an unexpected manner. This reaction did not take place at the esteric group, but hydrazine hydrate caused the opening of furan ring giving rise to hydrazide of 3-hydroxy-5-ethoxycarbonyl-2-pyrrolylacetic acid (**VIII**) (Scheme 3).

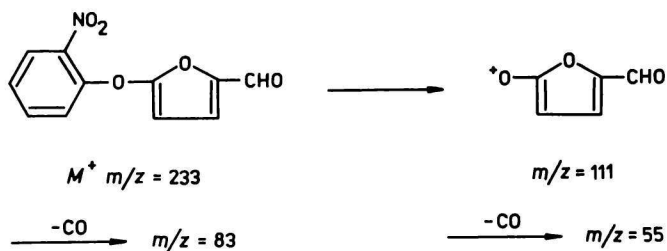
The IR spectra of **I—III** revealed characteristic bands  $\nu_{\text{as}}(\text{NO}_2)$  at  $\tilde{\nu} = 1538\text{—}1491\text{ cm}^{-1}$  and  $\nu_{\text{s}}(\text{NO}_2)$  at  $\tilde{\nu} = 1360\text{—}1346\text{ cm}^{-1}$ . The IR spectra of **II**, **III**, and **V** showed the absorption band of  $\text{C}\equiv\text{N}$  vibrations at  $\tilde{\nu} = 2225\text{—}2210\text{ cm}^{-1}$ ; absorption band of  $\text{C}=\text{O}$  group of the synthesized compounds being at  $\tilde{\nu} = 1726\text{—}1649\text{ cm}^{-1}$ . The IR spectrum of **VI** showed characteristic band of  $\text{N}_3$  group at  $\tilde{\nu} = 2110\text{ cm}^{-1}$  and **VIII** revealed two absorption bands of  $\text{C}=\text{O}$  groups at  $\tilde{\nu} = 1669\text{ cm}^{-1}$  and  $1639\text{ cm}^{-1}$  and absorption bands  $\nu(\text{OH})$  at  $\tilde{\nu} = 3442\text{ cm}^{-1}$  and  $\nu(\text{NH})$  at  $\tilde{\nu} = 3313\text{ cm}^{-1}$ .

The UV spectra of all synthesized compounds display an intense absorption band at  $\lambda = 250\text{—}380\text{ nm}$  and series of weaker bands at  $\lambda = 200\text{—}210\text{ nm}$ . Relatively high values  $\lambda_{\text{max}}$  of **II—VI** correspond with an extension of the conjugated system.

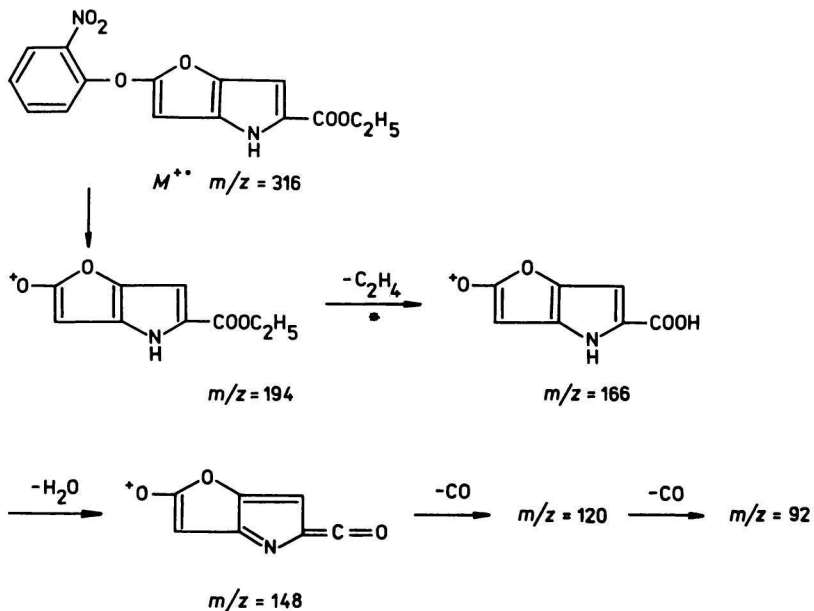
The  $^1\text{H NMR}$  spectra evidenced the structure of these compounds. The  $^1\text{H NMR}$  spectra of **I—VI** have signals of protons C-3—H and C-4—H of the furan ring. The formation of condensed products **II**, **III**, **IV**, and **VI** was confirmed by downfield shift of  $\text{C}_A\text{—H}$  or its disappearance in the case of **V**. The structure of **VII** was proved by proton signals which were attributed according to characteristic interaction of furopyrrole protons with long range interaction constant between C-3—H and C-6—H  $J_{3,6} = 0.75\text{ Hz}$ . A rise of **VIII** was confirmed by the disappearance of C-3—H signal of furo[3,2-*b*]pyrrole system and the signals of 2-nitrophenyl residue as well.

Mass spectra of compounds *I*, *V*, *VI*, *VII*, and *VIII* are introduced in Experimental.

The main fragmentation pattern involves a cleavage of 2-nitrophenyl ion to give rise to fragmentation ion with the highest intensity. The main fragmentation pathway of *I* and *VII* is shown in Schemes 4 and 5.



Scheme 4



Scheme 5

## Experimental

The IR spectra were measured in chloroform with a Specord 71 IR (Zeiss, Jena) spectrophotometer, compounds *IV* and *VIII* were measured using KBr technique (1 mg/g KBr). The electronic spectra were taken with a Specord UV VIS (Zeiss, Jena) apparatus. Measuring range  $\lambda = 200\text{--}600$  nm, concentration  $3 \times 10^{-5}\text{--}7 \times 10^{-5}$  mol dm<sup>-3</sup> in methanol at room temperature. The <sup>1</sup>H NMR spectra were recorded with a Tesla BS 487 C apparatus operating at 80 MHz. Hexamethyldisiloxane was used as internal reference. The electron impact mass spectra of compounds *I*, *V*—*VIII* were measured with an MS 902 S (AEI Manchester) apparatus at an ionizing electron energy 70 eV, trap current 100  $\mu$ A and the ionization chamber temperature 80 °C. Peaks of relative intensity  $\geq 5$  were omitted.

### 5-(2-Nitrophenoxy)-2-furaldehyde (*I*)

To melted 5-bromo-2-furaldehyde (17.5 g; 0.1 mol) sodium 2-nitrophenoxide (16.11 g; 0.1 mol) in dimethyl sulfoxide (50 cm<sup>3</sup>) was added at 90 °C. The reaction mixture was stirred at 90 °C for 7 h and poured into ice water (1 dm<sup>3</sup>). The separated precipitate was filtered off and distilled with the water stream (to remove the unreacted 5-bromo-2-furaldehyde). The residue was filtered off; yield 12.25 g (52.5 %), m.p. = 83—84 °C (ethanol).

For C<sub>11</sub>H<sub>7</sub>NO<sub>5</sub> (*M<sub>r</sub>* = 233.2) *w<sub>i</sub>*(calculated): 56.66 % C, 3.03 % H, 6.00 % N; *w<sub>i</sub>*(found): 56.54 % C, 2.98 % H, 6.00 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 1671 (C=O), 1520 ((NO<sub>2</sub>)<sub>as</sub>), 1352 ((NO<sub>2</sub>)<sub>s</sub>). UV —  $\lambda_{\max}/\text{nm}$  (log ( $\epsilon/(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$ )): 208 (3.13), 296 (3.33). <sup>1</sup>H NMR — (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 9.40 (1H, s, C<sub>A</sub>—H), 7.23 (1H, d, C-3—H), 5.73 (1H, d, C-4—H), 8.11—7.28 (4H, m, H<sub>arom</sub>), *J*<sub>3,4</sub> = 3.75 Hz. Mass spectrum — *m/z* (*I<sub>r</sub>*/%) : 233 (9.52), 123 (9.52), 122 (15.5), 111 (100), 106 (15.5), 83 (57.1).

### 2-Cyano-3-[5-(2-nitrophenoxy)-2-furyl]acrylonitrile (*II*)

To *I* (2.38 g; 0.01 mol) in methanol (20 cm<sup>3</sup>) the malonic acid dinitrile (0.78 g; 0.01 mol) and 10 % sodium ethoxide (5 drops) were added. The reaction mixture was stirred for 1 h. The separated precipitate was filtered off; yield 0.84 g (30.0 %), m.p. = 126—127 °C (ethanol).

For C<sub>14</sub>H<sub>7</sub>N<sub>3</sub>O<sub>4</sub> (*M<sub>r</sub>* = 281.2) *w<sub>i</sub>*(calculated): 59.79 % C, 2.51 % H, 14.94 % N; *w<sub>i</sub>*(found): 59.68 % C, 2.42 % H, 15.15 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 2220 (CN), 1525 ((NO<sub>2</sub>)<sub>as</sub>), 1346 ((NO<sub>2</sub>)<sub>s</sub>). UV —  $\lambda_{\max}/\text{nm}$  (log ( $\epsilon/(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$ )): 208 (3.36), 379 (3.59). <sup>1</sup>H NMR — (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 7.25 (1H, s, C<sub>A</sub>—H), 7.32 (1H, d, C-3—H), 5.84 (1H, d, C-4—H), 8.19—7.35 (4H, m, H<sub>arom</sub>), *J*<sub>3,4</sub> = 3.85 Hz.

### Methyl 2-cyano-3-[5-(2-nitrophenoxy)-2-furyl]acrylate (*III*)

*I* (1.16 g; 0.005 mol) in ethanol (15 cm<sup>3</sup>), methyl cyanoacetate (0.5 g; 0.005 mol), and 10 % sodium ethoxide (3 drops) were stirred for 1 h. The separated precipitate was filtered off; yield 1.37 g (87.3 %), m.p. = 157—158 °C (ethanol).

For  $C_{15}H_{10}N_2O_6$  ( $M_r = 314.2$ )  $w_i$ (calculated): 57.33 % C, 3.21 % H, 8.92 % N;  $w_i$ (found): 57.20 % C, 3.09 % H, 9.05 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 2210 (CN), 1726 (CO), 1497 ((NO<sub>2</sub>)<sub>as</sub>), 1346 ((NO<sub>2</sub>)<sub>s</sub>). UV —  $\lambda_{\max}/\text{nm}$  ( $\log(\epsilon/(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}))$ ): 208 (3.23), 370 (3.43). <sup>1</sup>H NMR — (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 7.81 (1H, s, C<sub>A</sub>—H), 7.35 (1H, d, C-3—H), 5.85 (1H, d, C-4—H), 8.17—7.37 (4H, m, H<sub>arom</sub>), 3.90 (3H, s, OCH<sub>3</sub>),  $J_{3,4} = 3.85$  Hz.

### 5-(2-Nitrophenoxy)-2-furaldehydoxime (IVa)

To the mixture of *I* (2.33 g; 0.01 mol), pyridine (10 cm<sup>3</sup>), and hydroxylammonium chloride (1.0 g; 0.015 mol) acetanhydride (6.0 g; 0.045 mol) was added under stirring at 25 °C. The reaction mixture was kept under these conditions for 3 h and then it was poured on ice (500 g). The separated precipitate was filtered off and washed with cold water; yield 1.54 g (62.3 %), m.p. = 126—127 °C (CCl<sub>4</sub>).

For  $C_{11}H_8N_2O_5$  ( $M_r = 248.2$ )  $w_i$ (calculated): 53.23 % C, 3.25 % H, 11.29 % N;  $w_i$ (found): 53.05 % C, 3.12 % H, 11.53 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 1583 (C=N), 1522 ((NO<sub>2</sub>)<sub>as</sub>), 1346 ((NO<sub>2</sub>)<sub>s</sub>), 3243 (OH). <sup>1</sup>H NMR — (DMSO-*d*<sub>6</sub>)  $\delta/\text{ppm}$ : 7.67 (1H, s, C<sub>A</sub>—H), 7.64 (1H, d, C-3—H), 6.02 (1H, d, C-4—H), 8.26—7.50 (4H, m, H<sub>arom</sub>),  $J_{3,4} = 3.5$  Hz.

### 5-(4-Nitrophenoxy)-2-furaldehydoxime (IVb)

*I* (1.14 g; 0.005 mol) in ethanol (20 cm<sup>3</sup>), hydroxylammonium chloride (0.5 g; 0.007 mol), and sodium acetate (0.55 g; 0.007 mol) were kept during 30 min at 70 °C. The reaction mixture was concentrated to a half-volume. The separated precipitate was filtered off; yield 0.9 g (72.1 %), m.p. = 139—140 °C (ethanol).

For  $C_{11}H_8N_2O_5$  ( $M_r = 248.2$ )  $w_i$ (calculated): 53.23 % C, 3.25 % H, 11.29 % N;  $w_i$ (found): 53.38 % C, 3.32 % H, 11.1 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 1572 (C=N), 1538 ((NO<sub>2</sub>)<sub>as</sub>), 1355 ((NO<sub>2</sub>)<sub>s</sub>). <sup>1</sup>H NMR — (DMSO-*d*<sub>6</sub>)  $\delta/\text{ppm}$ : 7.92 (1H, s, C<sub>A</sub>—H), 6.75 (1H, d, C-3—H), 6.08 (1H, d, C-4—H), 8.39—8.28 and 7.41—7.29 (4H, m, H<sub>arom</sub>),  $J_{3,4} = 3.45$  Hz.

Similarly was prepared the next compound.

### 5-(3-Nitrophenoxy)-2-furaldehydoxime (IVc)

Yield 0.8 g (64 %), m.p. = 153—154 °C (ethanol). For  $C_{11}H_8N_2O_5$  ( $M_r = 248.2$ )  $w_i$ (calculated): 53.23 % C, 3.25 % H, 11.29 % N;  $w_i$ (found): 53.42 % C, 3.40 % H, 11.01 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 1580 (C=N), 1535 ((NO<sub>2</sub>)<sub>as</sub>), 1360 ((NO<sub>2</sub>)<sub>s</sub>). <sup>1</sup>H NMR — (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta/\text{ppm}$ : 7.79 (1H, s, C<sub>A</sub>—H), 7.14 (1H, d, C-3—H), 5.79 (1H, d, C-4—H), 8.16—7.49 (4H, m, H<sub>arom</sub>),  $J_{3,4} = 3.5$  Hz.

## 5-(2-Nitrophenoxy)-2-furylcyaniide (V)

To the mixture of *I* (23.31 g; 0.1 mol), pyridine (78 cm<sup>3</sup>), and hydroxylammonium chloride (12 g; 0.17 mol) acetanhydride (55 cm<sup>3</sup>; 0.5 mol) was added under stirring at 95 °C. The reaction mixture was kept at 85–95 °C for 2 h, cooled and poured on ice. The separated precipitate was filtered off, yield 20.93 g (91 %), m.p. = 49 °C (ethanol).

For C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> (*M<sub>r</sub>* = 230.2) *w<sub>i</sub>*(calculated): 57.32 % C, 2.63 % H, 12.17 % N; *w<sub>i</sub>*(found): 57.22 % C, 2.50 % H, 12.22 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 2225 (CN), 1524 ((NO<sub>2</sub>)<sub>as</sub>), 1347 ((NO<sub>2</sub>)<sub>s</sub>). UV —  $\lambda_{\max}/\text{nm}$  (log ( $\epsilon/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ )): 207 (3.03), 256 (3.33). <sup>1</sup>H NMR — (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 7.10 (1H, d, C-3—H), 5.67 (1H, d, C-4—H), 8.12–7.22 (4H, m, H<sub>arom</sub>), *J*<sub>3,4</sub> = 3.7 Hz. Mass spectrum *m/z* (*I<sub>r</sub>*/%) : 230 (11.5), 123 (50), 122 (65), 108 (100), 106 (12.5), 80 (22.5), 54 (57.5).

## Ethyl 2-azido-3-[5-(2-nitrophenoxy)-2-furyl] acrylate (VI)

A solution of *I* (2.16 g; 0.01 mol) and ethyl azidoacetate (10.3 g; 0.08 mol) in ethanol (20 cm<sup>3</sup>) was added to sodium metal (1.84 g; 0.08 gat) dissolved in ethanol (60 cm<sup>3</sup>) at 5 °C. The mixture was stirred at 10 °C for 1 h, then ammonium chloride (4 g) in water (20 cm<sup>3</sup>) was added and after 10 min the solution was poured into cold water (400 cm<sup>3</sup>). The separated precipitate was filtered off, yield 2.17 g (63.2 %), m.p. = 71.5–72.0 °C (ethanol).

For C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>6</sub> (*M<sub>r</sub>* = 344.3), *w<sub>i</sub>*(calculated): 52.33 % C, 3.51 % H, 16.27 % N; *w<sub>i</sub>*(found): 52.19 % C, 3.42 % H, 16.44 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 2110 (N<sub>3</sub>), 1711 (C=O), 1524 ((NO<sub>2</sub>)<sub>as</sub>), 1347 ((NO<sub>2</sub>)<sub>s</sub>). UV —  $\lambda_{\max}/\text{nm}$  (log ( $\epsilon/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ )): 208 (3.24), 345 (3.53). <sup>1</sup>H NMR — (C<sub>6</sub>D<sub>6</sub>)  $\delta/\text{ppm}$ : 6.63 (1H, s, C<sub>A</sub>—H), 6.82 (1H, d, C-3—H), 5.33 (1H, d, C-4—H), 7.46–6.47 (4H, m, H<sub>arom</sub>), *J*<sub>3,4</sub> = 3.7 Hz, 3.90 (2H, q, —CH<sub>2</sub>—), 0.88 (3H, t, CH<sub>3</sub>). Mass spectrum — *m/z* (*I<sub>r</sub>*/%) : 344 (20), 194 (22.7), 139 (31.8), 123 (54.5), 122 (100), 106 (22.7).

Ethyl 2-(2-nitrophenoxy)-4H-furo[3,2-*b*]pyrrole-5-carboxylate (VII)

Ester VI (5.5 g; 0.016 mol) in toluene (500 cm<sup>3</sup>) was heated with stirring under reflux for 11/2 h. The solvent was distilled off under reduced pressure and the residue was purified by chromatography (silicagel—benzene), yield 3.3 g (65.2 %), m.p. = 153–154 °C (benzene).

For C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub> (*M<sub>r</sub>* = 316.3) *w<sub>i</sub>*(calculated): 56.96 % C, 3.82 % H, 8.86 % N; *w<sub>i</sub>*(found): 57.02 % C, 3.91 % H, 8.80 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 3477 (NH), 1685 (C=O), 1521 ((NO<sub>2</sub>)<sub>as</sub>), 1346 ((NO<sub>2</sub>)<sub>s</sub>). UV —  $\lambda_{\max}/\text{nm}$  (log ( $\epsilon/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ )): 210 (3.21), 250 (3.09), 306 (3.59). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta/\text{ppm}$ : 11.86 (1H, s, NH), 6.77 (1H, d, C-6—H), 6.21 (1H, d, C-3—H), 8.18–7.30 (4H, m, H<sub>arom</sub>), *J*<sub>3,6</sub> = 0.75 Hz, 4.25 (2H, q-CH<sub>2</sub>), 1.29 (3H, t, CH<sub>3</sub>). Mass spectrum — *m/z* (*I<sub>r</sub>*/%) : 194 (100), 166 (21.6), 148 (43.2), 92 (10.8), 78 (10.8), 53 (27).



*5-Ethoxycarbonyl-5-hydroxy-2-pyrrolylacethydrazide (VIII)*

80 % hydrazine hydrate (1.8 cm<sup>3</sup>) was added to a solution of VII (0.32 g; 0.001 mol) in ethanol (20 cm<sup>3</sup>), the mixture was refluxed for 2 h and separated crystals were filtered off after cooling, yield 0.16 g (71.4 %), m.p. = 203—204 °C (ethanol).

For C<sub>9</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub> (M<sub>r</sub> = 227.2) w<sub>i</sub>(calculated): 47.58 % C, 5.77 % H, 18.50 % N; w<sub>i</sub>(found): 47.42 % C, 5.65 % H, 18.40 % N. IR —  $\tilde{\nu}_{\max}/\text{cm}^{-1}$ : 1669 (C=O), 3442 (OH), 3313 (NH). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta/\text{ppm}$ : 6.20 (1H, s, C-4—H), 4.18 (2H, q-CH<sub>2</sub>), 3.35 (2H, s, OC—CH<sub>2</sub>), 1.22 (3H, t, CH<sub>3</sub>). Mass spectrum — m/z (I, %): 227 (40), 181 (33.3), 168 (80), 140 (50), 122 (100), 94 (33.3), 68 (13.3), 53 (13.3), 44 (26.6).

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