

# Synthesis and reactions of 2-aryloxy- and 2-arylthiofuro[3,2-*b*]pyrrole derivatives

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The preparation of 5-(2-nitrophenylthio)-2-furaldehyde and its reactions with compounds containing an active methylene group and with hydroxylammonium chloride are described. Starting from corresponding furaldehydes 2-aryloxy- and 2-arylthiofuro[3,2-*b*]pyrrole derivatives were prepared and their reactions were studied.

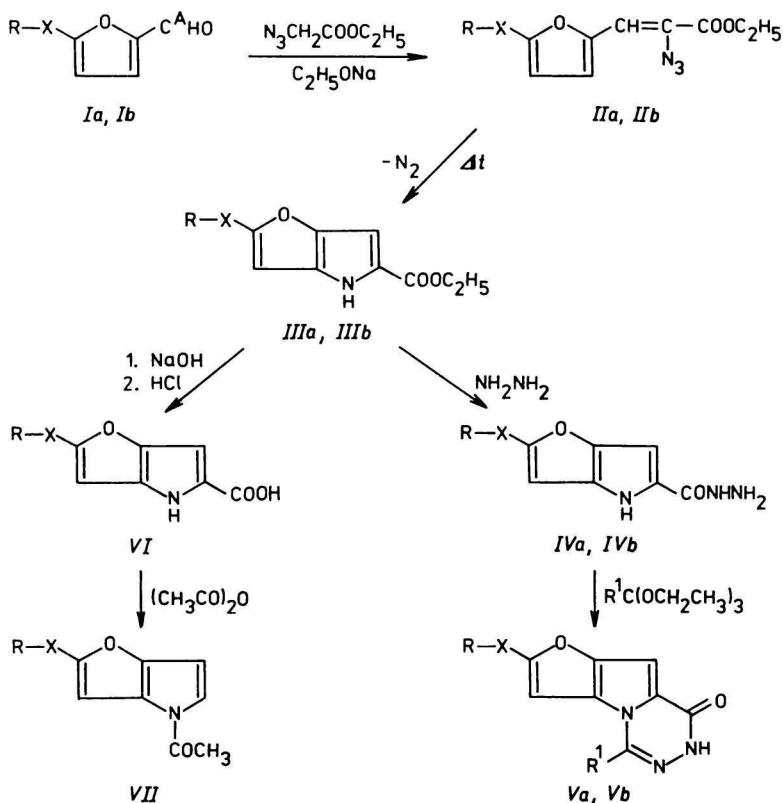
Описано получение 5-(2-нитрофенилтио)-2-фуральдегида и его реакции с соединениями с реакционноспособной метиленовой группой и с солянокислым гидроксиламином. Исходя из соответствующих фуральдегидов были синтезированы производные 2-арилокси- и 2-арилтиофуоро[3,2-*b*]пиррола и были исследованы их реакции.

Our preceding papers [1, 2] deal with the synthesis of substituted 5-phenoxy-2-furaldehydes as heterocyclic analogues of diphenyl ethers, to which, in the last few years in the area of novel chemical means with herbicidal activity, considerable attention has been paid [3—8].

As a continuation of our previous study [1] we tried to get a deeper insight into the reactivity of furo[3,2-*b*]pyrroles having aryloxy and arylthio group in position 2.

The starting 5-(4-chloro-2-methylphenoxy)- or 5-(2-nitrophenylthio)-2-furaldehyde (*Ia*, *Ib*) were prepared by reaction of 5-bromo-2-furaldehyde with sodium 4-chloro-2-methylphenoxide resp. 2-nitrophenylthiolate in dimethyl sulfoxide. The yield of this reaction was influenced by features of substituents attached to the benzene ring. Compound *Ia* was obtained in 92 % [2] and *Ib* in 34 % yield. The lower yield of *Ib* lies in weaker nucleophilicity of corresponding 2-nitrophenylthiolate anion due to the electron-withdrawing nitro group.

The prepared aldehydes *Ia*, *Ib* reacted with ethyl azidoacetate giving, in the presence of sodium ethoxide, 3-substituted 2-azidopropenoates (*IIa*, *IIb*) which represent the highly reactive azides of vinyl type. The thermolysis of these compounds leads to ethyl 2-(4-chloro-2-methylphenoxy)- or 2-(2-nitrophenylthio)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (*IIIa*, *IIIb*). The corresponding hydrazides *IVa*, *IVb* (Scheme 1) were obtained by reacting *IIIa*, *IIIb* with hydrazine



For *Ia-Va, Vb, VI, VII*  $\text{X} = \text{O}$ ,  $\text{R} = 4\text{-chloro-2-methylphenyl}$ .  
 For *Ib-IVb*  $\text{X} = \text{S}$ ,  $\text{R} = 2\text{-nitrophenyl}$   $\text{R}^1 = \text{H}, \text{CH}_3$ .

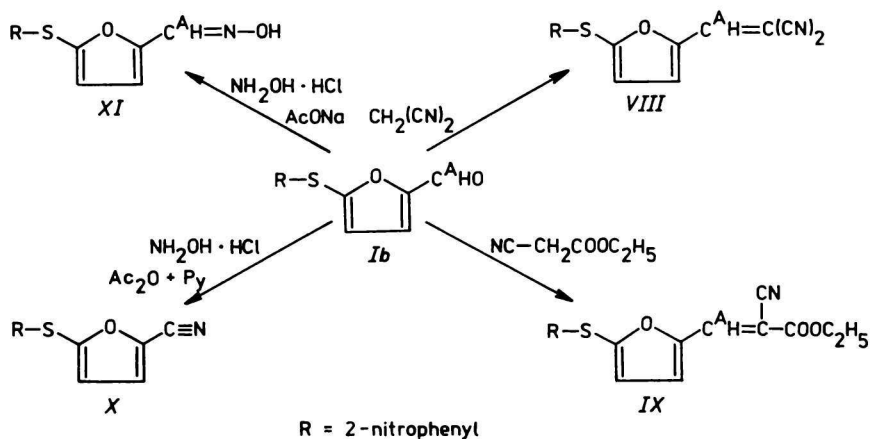
Scheme 1

hydrate in excess in ethanol. It is interesting to remark that ethyl 2-(2-nitrophenoxy)-4*H*-furo[3,2-*b*]pyrrole-5-carboxylate reacted with hydrazine in an unexpected manner [1]. This reaction did not take place at the ethoxycarbonyl group, but hydrazine caused the opening of furan ring giving rise to hydrazide of 3-hydroxy-5-ethoxycarbonyl-2-pyrrolylacetic acid [1].

Two reaction centres of hydrazide *IVa* enable to carry out a cyclization reaction with triethyl orthoformate or orthoacetate giving rise to compounds *Va, Vb* having attached 1,2,4-triazine ring to furo[3,2-*b*]pyrrole system (Scheme 1). Hydrolysis of ester *IIIa* gave corresponding acid (*VI*) which was used for the preparation of 4-acetyl derivative (*VII*). Compound *VI* is a suitable

material for the synthesis of further derivatives and for the study of the reactions with dienophiles [9].

The new synthesized 5-(2-nitrophenylthio)-2-furaldehyde was followed in some condensation reactions with the aim to compare its behaviour with that of 5-(2-nitrophenoxy)-2-furaldehyde which afforded in the reaction with hydroxylammonium chloride in the presence of sodium acetate an anomalous product [1]. We found out indeed the normal behaviour of *Ib* in the above-mentioned conditions giving the corresponding oxime (*XI*). Also in other condensation reactions the normal products were formed. The reaction of *Ib* with propanedinitrile afforded 5-(2-nitrophenylthio)-2-furfurylidenepropanedinitrile (*VIII*), with ethyl cyanoacetate substituted ethyl 2-cyano-3-[5-(2-nitrophenylthio)-2-furyl]propenoate (*IX*) was formed. If the reaction with hydroxylammonium chloride was performed in acetic anhydride in the presence of pyridine at 90 °C 5-(2-nitrophenylthio)-2-furyl cyanide (*X*) was obtained (Scheme 2).



Scheme 2

The structure of synthesized compounds was confirmed by spectral methods using the knowledge from Ref. [1, 10–12]. <sup>1</sup>H NMR spectra of compounds *Ib*, *IIa*, *IIb*, *VIII*–*XI* exhibited H-3 and H-4 proton signals of the furan ring at  $\delta = 7.06$ – $8.12$  ppm and  $5.49$ – $7.31$  ppm with a coupling constant  $J_{3,4} = 2.1$ – $4.0$  Hz. The formation of condensed products *VII*, *IX*, *X* was confirmed by the downfield shift of C<sup>A</sup>–H signal or its disappearance in the case of *XI*. A rise of *IIa*, *IIb* was confirmed by the presence of H-6 of the pyrrole ring and by the shift of H-3 of furo[3,2-*b*]pyrrole system. In *IIIa*, *IIIb*, *IVa*, *IVb*, *VI* there is a long-range coupling constant between H-3 and H-6 protons  $J_{3,6} = 0.7$ –

1.1 Hz. The structure of hydrazides *IVa*, *IVb* and acid *VI* was proved by the missing of  $C_2H_5$  group signals and by a change of H-3 and H-6 signal position. Formation of 1,2,4-triazine derivatives *Va*, *Vb* was backed by the presence of H-4 ( $\delta = 8.55$  ppm) or C-4— $CH_3$  ( $\delta = 2.47$  ppm) signals. The compound *VII* exhibited besides the long-range interaction  $J_{3,6} = 0.7$  Hz, the interaction  $J_{5,6} = 4.0$  Hz.

The IR spectra of *Ib*, *IIB*, *IIIb*, and *VIII—XI* revealed bands of the vibrations  $\nu_{as}(NO_2)$  at  $\tilde{\nu} = 1500—1520$   $cm^{-1}$  and  $\nu_s(NO_2)$  at  $\tilde{\nu} = 1320—1350$   $cm^{-1}$ . The IR spectra of *VIII—X* showed the absorption band of  $C\equiv N$  vibrations at  $\tilde{\nu} = 2210—2220$   $cm^{-1}$ ; absorption band of  $C=O$  group of the synthesized compounds being at  $\tilde{\nu} = 1590—1690$   $cm^{-1}$ . The IR spectrum of *IIa*, *IIB* showed a characteristic band of  $N_3$  group at  $\tilde{\nu} = 2050—2100$   $cm^{-1}$  and  $\nu(NH)$  at  $\tilde{\nu} = 3450—3480$   $cm^{-1}$ .

The UV spectra of all synthesized compounds display an intense absorption band at  $\lambda_{max} = 300—320$  nm and a further band at 205—250 nm. Relatively high values  $\lambda_{max}$  of *Va* correspond with an extension of the conjugated system.

In conclusion we can state that the investigated systems, bearing 4-chloro-2-methylphenoxy and 2-nitrophenylthio substituents in C-2 of furo[3,2-*b*]pyrrole or C-5 of furan rings, behave differently from their 2-nitrophenoxy analogues. This difference can be explained by the effect of the electron-withdrawing 2-nitrophenoxy group, creating the conditions for a rise of the anomalous reaction products.

## Experimental

The IR spectra were measured on a Specord 71 IR (Zeiss, Jena) spectrophotometer using KBr technique (1 mg/300 mg KBr). The electronic spectra of dioxane (*IIIa*, *IIIb*, *IVa*, *VI*) or methanol solutions of compounds ( $c = (1—9) \times 10^{-5}$  mol  $dm^{-3}$ ) were taken with Specord UV VIS (Zeiss, Jena) apparatus in the range  $\lambda = 200—800$  nm at room temperature. The  $^1H$  NMR spectra of hexadeuterodimethyl sulfoxide or deuteriochloroform solutions of compounds were recorded with a Tesla BS 487 C instrument, hexamethyldisiloxane and tetramethylsilane being the reference.

The starting compounds were prepared from 5-bromo-2-furaldehyde according to [13] and 5-(4-chloro-2-methylphenoxy)-2-furaldehyde (*Ia*) according to [2].

### 5-(2-Nitrophenylthio)-2-furaldehyde (*Ib*)

To sodium 2-nitrophenylthiolate (17.7 g; 0.1 mol) in dimethyl sulfoxide (40  $cm^3$ ), 5-bromo-2-furaldehyde (17.5 g; 0.1 mol) in dimethyl sulfoxide (10  $cm^3$ ) was dropped under stirring at 90 °C. The reaction mixture was stirred at 90 °C for 7 h and poured into ice water. The separated precipitate was filtered off and distilled with water steam. After

cooling the residue was filtered off. Yield = 8.47 g (34 %), m.p. = 83–85 °C (ethanol). For  $C_{11}H_7NO_4S$  ( $M_r = 249.5$ )  $w_i$ (calc.): 53.02 % C, 2.83 % H, 5.62 % N, 12.86 % S;  $w_i$ (found): 52.94 % C, 2.75 % H, 5.52 % N, 12.68 % S.  $^1H$  NMR spectrum ( $CDCl_3$ ),  $\delta$ /ppm: 9.68 (1H, s, CH=O), 7.36–7.58 (4H, m,  $H_{arom}$ ), 7.33 (1H, d, H-3), 6.95 (1H, d, H-4),  $J_{3,4} = 3.8$  Hz. IR spectrum (KBr),  $\tilde{\nu}/cm^{-1}$ : 1690 ( $\nu(C=O)$ ), 1520 ( $\nu_{as}(NO_2)$ ), 1350 ( $\nu_s(NO_2)$ ). UV spectrum (methanol),  $\lambda_{max}/nm$  (log  $\{\epsilon\}$ ): 313 (3.04), 228 (3.01).

### *Ethyl 2-azido-3-(5-RX-2-furyl)propenoates IIa, IIb*

The solution of *Ia* (3.47 g; 0.01 mol) and ethyl azidoacetate (10.32 g; 0.08 mol) in ethanol (25 cm<sup>3</sup>) was added at 0 °C during 30 min to solution of sodium ethoxide (prepared from sodium metal (1.84 g; 0.08 mol) in ethanol (60 cm<sup>3</sup>)). Stirring was continued for additional 60 min at 0–5 °C, then the reaction mixture was cooled to 0 °C, ammonium chloride (4 g, 25 cm<sup>3</sup> of H<sub>2</sub>O) was added and poured in an ice. The separated precipitate of 5-(4-chloro-2-methylphenoxy)-2-furyl derivative (*IIa*) was filtered off. Yield = 1.43 g (44 %), m.p. = 91–93 °C (ethanol). For  $C_{16}H_{14}ClN_3O_4$  ( $M_r = 347.8$ )  $w_i$ (calc.): 55.25 % C, 4.06 % H, 12.08 % N, 10.19 % Cl;  $w_i$ (found): 55.11 % C, 3.97 % H, 12.00 % N, 9.98 % Cl.  $^1H$  NMR spectrum ( $CDCl_3$ ),  $\delta$ /ppm: 7.04–7.30 (3H, m,  $H_{arom}$ ), 7.06 (1H, d, H-3), 6.75 (1H, d, H-A), 5.49 (1H, d, H-4), 4.30 (2H, q, CH<sub>2</sub>), 2.27 (3H, s, CH<sub>3</sub><sub>arom</sub>), 1.23 (3H, t, CH<sub>3</sub>),  $J_{3,4} = 3.5$  Hz,  $J_{4,A} = 0.5$  Hz. IR spectrum (KBr),  $\tilde{\nu}/cm^{-1}$ : 1690 ( $\nu(C=O)$ ), 1510 ( $\nu_{as}(NO_2)$ ), 1340 ( $\nu_s(NO_2)$ ), 2050 ( $\nu(N_3)$ ).

Similarly from *Ib* was prepared 5-(2-nitrophenylthio)-2-furyl derivative (*IIb*). Yield = 40 %, m.p. = 104–105 °C (ethanol). For  $C_{15}H_{12}N_4O_5S$  ( $M_r = 360.3$ )  $w_i$ (calc.): 50.00 % C, 3.36 % H, 15.55 % N, 8.88 % S;  $w_i$ (found): 49.91 % C, 3.24 % H, 15.50 % N, 8.72 % S.  $^1H$  NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ /ppm: 7.27–8.20 (4H, m,  $H_{arom}$ ), 7.22 (1H, d, H-3), 7.20 (1H, d, H-4), 6.71 (1H, s, H-A), 4.23 (2H, q, CH<sub>2</sub>), 1.22 (3H, t, CH<sub>3</sub>),  $J_{3,4} = 3.5$  Hz. IR spectrum (KBr),  $\tilde{\nu}/cm^{-1}$ : 1700 ( $\nu(C=O)$ ), 1510 ( $\nu_{as}(NO_2)$ ), 1330 ( $\nu_s(NO_2)$ ), 2100 ( $\nu(N_3)$ ). UV spectrum (methanol),  $\lambda_{max}/nm$  (log  $\{\epsilon\}$ ): 320 (3.69), 207 (3.49).

### *Ethyl 4H-2-RX-furo[3,2-*b*]pyrrole-5-carboxylate IIIa, IIIb*

The compound *IIa* (9.71 g; 0.028 mol) dissolved in toluene (700 cm<sup>3</sup>) was heated under reflux and stirring for 2 h, the solvent was evaporated *in vacuo* and 2-(4-chloro-2-methylphenoxy) derivative (*IIIa*) was crystallized. Yield = 3.58 g (40 %), m.p. = 110–111 °C (ethanol). For  $C_{16}H_{14}ClNO_4$  ( $M_r = 319.7$ )  $w_i$ (calc.): 60.11 % C, 4.41 % H, 4.38 % N, 11.08 % Cl;  $w_i$ (found): 60.02 % C, 4.34 % H, 4.54 % N, 10.87 % Cl.  $^1H$  NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ /ppm: 11.70 (1H, s, NH), 6.10–7.40 (3H, m,  $H_{arom}$ ), 6.65 (1H, d, H-6), 5.87 (1H, d, H-3), 4.10 (2H, q, CH<sub>2</sub>), 2.27 (3H, s, CH<sub>3</sub><sub>arom</sub>), 1.20 (3H, t, CH<sub>3</sub>),  $J_{3,6} = 0.70$  Hz. IR spectrum (KBr),  $\tilde{\nu}/cm^{-1}$ : 1675 ( $\nu(C=O)$ ), 3480 ( $\nu(NH)$ ). UV spectrum (dioxane),  $\lambda_{max}/nm$  (log  $\{\epsilon\}$ ): 307 (3.06), 218 (2.88).

Analogically was prepared 2-(2-nitrophenylthio) derivative (*IIIb*). Yield = 37 %, m.p. = 166 °C (ethanol). For  $C_{15}H_{12}N_2O_5S$  ( $M_r = 332.3$ )  $w_i$ (calc.): 54.22 % C, 3.64 % H,

8.43 % N, 9.63 % S;  $w_i$ (found): 54.14 % C, 3.60 % H, 8.43 % N, 9.42 % S.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ /ppm: 11.45 (1H, s, NH), 7.32—8.00 (4H, m,  $\text{H}_{\text{arom}}$ ), 7.22 (1H, s, H-6), 6.72 (1H, s, H-3), 4.23 (2H, q,  $\text{CH}_2$ ), 1.25 (3H, t,  $\text{CH}_3$ ). IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1660 ( $\nu(\text{C}=\text{O})$ ), 3460 ( $\nu(\text{NH})$ ), 1515 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1340 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (dioxane),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 317 (3.59).

### 2-Substituted 4H-furo[3,2-b]pyrrole-5-carbohydrazide IVa, IVb

Solution of *IIIa* (3.47 g; 0.01 mol) in ethanol (50  $\text{cm}^3$ ) was refluxed with hydrazine hydrate (80 %; 20  $\text{cm}^3$ ) for 24 h. The separated solid of 2-(4-chloro-2-methylphenoxy) derivative (*IVa*) was filtered off. Yield = 2.14 g (70 %), m.p. = 221—223 °C (ethanol). For  $\text{C}_{14}\text{H}_{12}\text{ClN}_3\text{O}_3$  ( $M_r = 305.7$ )  $w_i$ (calc.): 55.00 % C, 3.96 % H, 13.75 % N, 11.60 % Cl;  $w_i$ (found): 54.91 % C, 3.84 % H, 13.92 % N, 11.33 % Cl.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ /ppm: 11.30 (1H, s, NH), 9.20 (1H, s, NH), 6.77—7.37 (3H, m,  $\text{H}_{\text{arom}}$ ), 6.71 (1H, d, H-6), 5.82 (1H, d, H-3), 4.25 (2H, s,  $\text{NH}_2$ ), 2.20 (3H, s,  $\text{CH}_{3\text{arom}}$ ),  $J_{3,6} = 0.90$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1620 ( $\nu(\text{C}=\text{O})$ ). UV spectrum (dioxane),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 304 (3.31), 208 (3.00).

2-(2-Nitrophenylthio) derivative (*IVb*) was prepared analogically. Yield = 52 %, m.p. = 246—247 °C (ethanol). For  $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4\text{S}$  ( $M_r = 318.2$ )  $w_i$ (calc.): 49.08 % C, 3.18 % H, 17.61 % N, 10.06 % S;  $w_i$ (found): 49.01 % C, 3.04 % H, 17.61 % N, 9.95 % S.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ /ppm: 11.40 (1H, s, NH), 9.51 (1H, s, NH), 7.25—8.00 (4H, m,  $\text{H}_{\text{arom}}$ ), 7.18 (1H, s, H-6), 6.78 (1H, s, H-3), 4.37 (2H, s,  $\text{NH}_2$ ). IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1625 ( $\nu(\text{C}=\text{O})$ ), 1517 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1340 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 227 (2.91), 314 (3.01).

### 7-(4-Chloro-2-methylphenoxy)-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-d]-[1,2,4]-triazin-1-one (Va) and its 4-methyl derivative Vb

The hydrazide *IVa* (3.05 g; 0.01 mol) and triethyl orthoformate (1.77 g; 0.012 mol) were refluxed in dimethylformamide (10  $\text{cm}^3$ ) for 2.5 h. After cooling the separated solid *Va* was filtered off. Yield = 1.83 g (58 %), m.p. = 247—249 °C (dimethylformamide). For  $\text{C}_{15}\text{H}_{10}\text{ClN}_3\text{O}_3$  ( $M_r = 315.7$ )  $w_i$ (calc.): 57.07 % C, 3.19 % H, 13.31 % N, 11.23 % Cl;  $w_i$ (found): 56.98 % C, 3.13 % H, 13.54 % N, 10.92 % Cl.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ /ppm: 8.55 (1H, s, H-4), 7.12—7.49 (3H, m,  $\text{H}_{\text{arom}}$ ), 7.06 (1H, d, H-9), 6.24 (1H, d, H-6), 2.20 (3H, s,  $\text{CH}_3$ ),  $J_{6,9} = 0.95$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1664 ( $\nu(\text{C}=\text{O})$ ). UV spectrum (dioxane),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 301 (3.26), 244 (3.42).

*Vb* was obtained from *IVa* and ethyl orthoacetate in an analogous way. Yield = 74 %, m.p. = 262—263 °C (dimethylformamide). For  $\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{O}_3$  ( $M_r = 329.7$ )  $w_i$ (calc.): 58.29 % C, 3.67 % H, 12.75 % N, 10.75 % Cl;  $w_i$ (found): 58.32 % C, 3.61 % H, 12.61 % N, 10.53 % Cl.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ /ppm: 7.05—7.55 (3H, m,  $\text{H}_{\text{arom}}$ ), 7.05 (1H, d, H-9), 6.46 (1H, d, H-6), 2.47 (3H, s, C-4— $\text{CH}_3$ ), 2.20 (3H, s,  $\text{CH}_{3\text{arom}}$ ),

$J_{6,9} = 1.10$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1665 ( $\nu(\text{C}=\text{O})$ ). UV spectrum (dioxane),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 303 (2.94), 238 (3.06).

*2-(4-Chloro-2-methylphenoxy)-4H-furo[3,2-b]pyrrole-5-carboxylic acid (VI)*

Sodium hydroxide (20  $\text{cm}^3$ , 5%) was added to the solution of the ester *IIIa* (3.19 g; 0.01 mol) in ethanol (20  $\text{cm}^3$ ). The solution was refluxed for 2 h, the separated sodium salt dissolved in the mixture ethanol—water ( $\phi_r = 1:1$ ), heated with charcoal, cooled and precipitated by addition of hydrochloric acid to a weak acid reaction. The separated solid was filtered off and washed with water. Yield = 1.45 g (50%), m.p. = 150 °C (ethanol). For  $\text{C}_{14}\text{H}_{10}\text{ClNO}_4$  ( $M_r = 291.7$ )  $w_i$ (calc.): 57.65% C, 3.46% H, 4.81% N, 12.15% Cl;  $w_i$ (found): 57.50% C, 3.42% H, 4.82% N, 11.87% Cl.  $^1\text{H}$  NMR spectrum ( $\text{DMSO-d}_6$ ),  $\delta/\text{ppm}$ : 11.50 (1H, s, NH), 6.87—7.32 (3H, m,  $\text{H}_{\text{arom}}$ ), 6.61 (1H, d, H-6), 5.86 (1H, d, H-3), 2.18 (3H, s,  $\text{CH}_3$ ),  $J_{3,6} = 0.99$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1690 ( $\nu(\text{C}=\text{O})$ ), 3450 ( $\nu(\text{NH})$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 304 (3.47), 205 (3.06).

*4-Acetyl-2-(4-chloro-2-methylphenoxy)furo[3,2-b]pyrrole (VII)*

The acid *VI* (1 g; 3.4 mmol) in acetic anhydride (15  $\text{cm}^3$ ) was refluxed under stirring for 4 h. Acetic anhydride was distilled off *in vacuo* and the residue of *VII* was crystallized. Yield = 1.16 g (39%), m.p. = 66—67 °C (methanol). For  $\text{C}_{15}\text{H}_{12}\text{ClNO}_3$  ( $M_r = 289.7$ )  $w_i$ (calc.): 62.19% C, 4.18% H, 4.84% N, 12.24% Cl;  $w_i$ (found): 62.32% C, 4.18% H, 4.85% N, 11.98% Cl.  $^1\text{H}$  NMR spectrum ( $\text{DMSO-d}_6$ ),  $\delta/\text{ppm}$ : 7.77 (1H, d, H-5), 6.86—7.36 (3H, m,  $\text{H}_{\text{arom}}$ ), 6.21 (1H, d, H-3), 5.99 (1H, dd, H-6), 2.50 (3H, s,  $\text{COCH}_3$ ), 2.25 (3H, s,  $\text{CH}_{3\text{arom}}$ ),  $J_{3,6} = 0.7$  Hz,  $J_{5,6} = 4.0$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1590 ( $\nu(\text{C}=\text{O})$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 285 (3.05), 240 (3.01).

*5-(2-Nitrophenylthio)-2-furfurylidenepropanedinitrile (VIII)*

To the compound *Ib* (2.49 g; 0.01 mol) in ethanol (60  $\text{cm}^3$ ) propanedinitrile (0.79 g; 0.012 mol) and sodium ethoxide in ethanol (5 drops, 10%) were added. The reaction mixture was stirred for 1 h at room temperature. The separated precipitate was filtered off. Yield = 2.85 g (96%), m.p. = 184—186 °C (ethanol). For  $\text{C}_{14}\text{H}_7\text{N}_3\text{O}_3\text{S}$  ( $M_r = 297.2$ )  $w_i$ (calc.): 56.58% C, 2.37% H, 14.14% N, 10.70% S;  $w_i$ (found): 56.43% C, 2.31% H, 13.96% N, 10.42% S.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta/\text{ppm}$ : 7.44—8.20 (4H, m,  $\text{H}_{\text{arom}}$ ), 8.20 (1H, s, H-A), 7.61 (1H, d, H-3), 7.14 (1H, d, H-4),  $J_{3,4} = 4.0$  Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 2210 ( $\nu(\text{C}\equiv\text{N})$ ), 1500 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1320 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  ( $\log \{\epsilon\}$ ): 234 (3.08), 372 (3.16).

*Ethyl 2-cyano-3-[5-(2-nitrophenylthio)-2-furyl]propenoate (IX)*

To the compound *Ib* (2.41 g; 0.01 mol) in ethanol (60 cm<sup>3</sup>), ethyl cyanoacetate (0.5 g; 0.05 mol) and sodium ethoxide in ethanol (3 drops, 10%) were added. The reaction mixture was stirred at room temperature for 1 h. The separated precipitate was filtered off. Yield = 0.83 g (24%), m.p. = 163—165 °C (ethanol). For C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>S (*M<sub>r</sub>* = 344.3) *w<sub>i</sub>*(calc.): 55.82% C, 3.51% H, 8.14% N, 9.30% S; *w<sub>i</sub>*(found): 55.63% C, 3.44% H, 7.94% N, 9.18% S. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ/ppm: 7.17—8.17 (4H, m, H<sub>arom</sub>), 8.08 (1H, s, H-A), 7.52 (1H, d, H-3), 7.19 (1H, d, H-4), 4.25 (2H, q, CH<sub>2</sub>), 1.25 (3H, t, CH<sub>3</sub>), *J*<sub>3,4</sub> = 3.5 Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1605 ( $\nu(\text{C}=\text{O})$ ), 2220 ( $\nu(\text{C}\equiv\text{N})$ ), 1500 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1320 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  (log { $\epsilon$ }): 212 (3.04), 361 (3.09).

*5-(2-Nitrophenylthio)-2-furyl cyanide (X)*

To the mixture of *Ib* (2.49 g; 0.01 mol), pyridine (8 cm<sup>3</sup>), and hydroxylammonium chloride (0.83 g; 0.012 mol) acetic anhydride (5.5 cm<sup>3</sup>; 0.05 mol) was added under stirring. The reaction mixture was kept at 85—95 °C for 2 h, cooled and poured on ice. The separated precipitate was filtered off. Yield = 1.23 g (50%), m.p. = 64—66 °C (ethanol). For C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>O<sub>3</sub>S (*M<sub>r</sub>* = 246.2) *w<sub>i</sub>*(calc.): 53.67% C, 2.46% H, 11.38% N, 13.00% S; *w<sub>i</sub>*(found): 53.72% C, 2.63% H, 10.98% N, 13.14% S. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ/ppm: 7.14—8.05 (4H, m, H<sub>arom</sub>), 6.95 (1H, d, H-3), 6.73 (1H, d, H-4), *J*<sub>3,4</sub> = 3.5 Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1605 ( $\nu(\text{C}=\text{O})$ ), 2220 ( $\nu(\text{C}\equiv\text{N})$ ), 1500 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1320 ( $\nu_{\text{s}}(\text{NO}_2)$ ). UV spectrum (methanol),  $\lambda_{\text{max}}/\text{nm}$  (log { $\epsilon$ }): 224 (3.01).

*5-(2-Nitrophenylthio)-2-furaldehyde oxime (XI)*

*Ib* (2.49 g; 0.01 mol) in ethanol (40 cm<sup>3</sup>), hydroxylammonium chloride (0.83 g; 0.012 mol), and sodium acetate (0.98 g; 0.012 mol) were refluxed for 1 h. The reaction mixture was concentrated to a half-volume. The separated precipitate was filtered off. Yield = 0.71 g (27%), m.p. = 133—135 °C (ethanol). For C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S (*M<sub>r</sub>* = 264.2) *w<sub>i</sub>*(calc.): 50.01% C, 3.05% H, 10.60% N, 12.11% S; *w<sub>i</sub>*(found): 50.12% C, 2.93% H, 10.37% N, 12.02% S. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ/ppm: 7.20—8.20 (4H, m, H<sub>arom</sub>), 8.01 (1H, s, H-A), 7.20 (1H, d, H-3), 6.81 (1H, s, H-4), *J*<sub>3,4</sub> = 3.5 Hz. IR spectrum (KBr),  $\tilde{\nu}/\text{cm}^{-1}$ : 1580 ( $\nu(\text{C}\equiv\text{N})$ ), 1510 ( $\nu_{\text{as}}(\text{NO}_2)$ ), 1355 ( $\nu_{\text{s}}(\text{NO}_2)$ ).

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