

REACTIONS OF 2-ARYL-4H-FURO[3,2-*b*]PYRROLE DERIVATIVES

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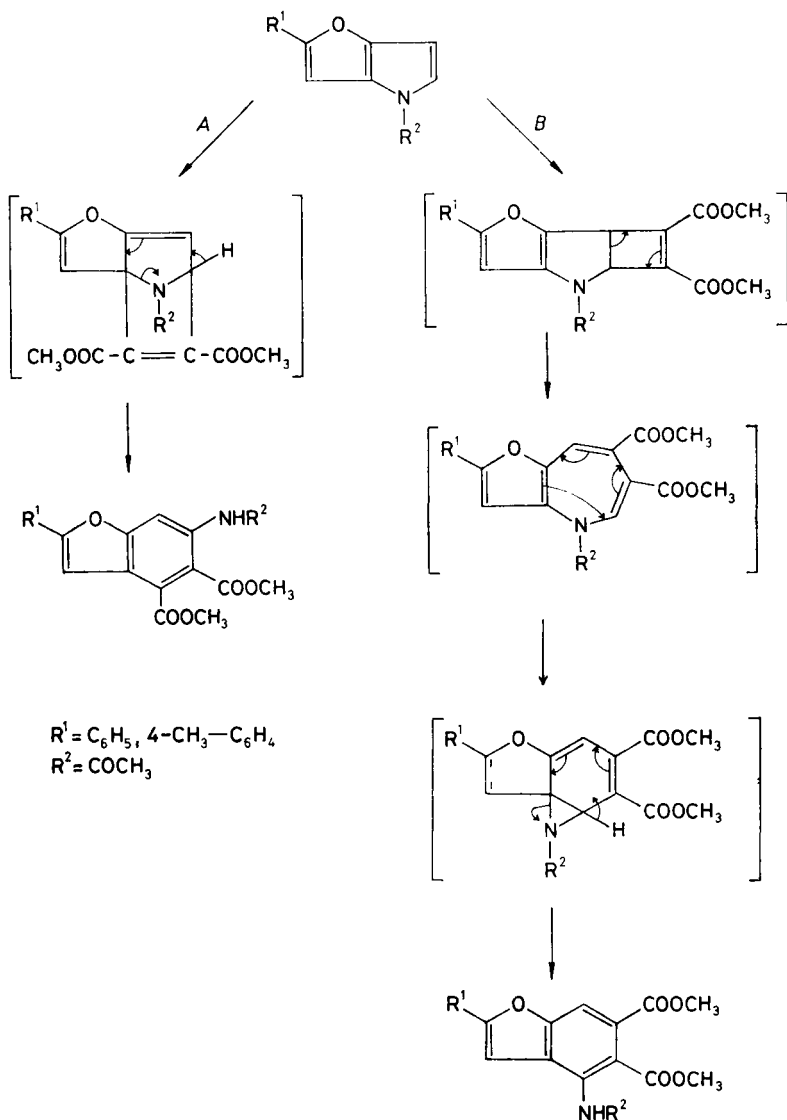
Preparation of 4-acetyl-2-arylfuro[3,2-*b*]pyrroles is described and reactions of 2-aryl-4H-furo[3,2-*b*]pyrrole and its substituted analogues with dimethyl butinedioate and some further reactions inevitable for the structure determination of compounds prepared were studied.

2-Pyrrole and 2-indolecarboxylic acids behaving as aminoacids react with acetic anhydride to give dioxopiperazines in an intermolecular dehydration<sup>1,2</sup>. 2-Aryl-4H-furo[3,2-*b*]pyrrole-5-carboxylic acids<sup>3</sup> did not afford the expected dimer at analogous reaction conditions, but underwent an acetylative decarboxylation to yield the corresponding 4-acetyl-2-arylfuro[3,2-*b*]pyrroles *Ia,b*. Since also ethyl esters of the above-mentioned acids furnished with acetic anhydride the acetylation products at nitrogen *IIa,b*, one can presume a mechanism, where acetylation takes place in the first step. The presence of an acetyl group at nitrogen of 2-aryl-4H-furo[3,2-*b*]pyrrole-5-carboxylic acids increases their acidity and consequently, also the temperature of the reaction medium becomes sufficient for decarboxylation.

Reactions of pyrroles and indoles with dimethyl butinedioate have been described<sup>4-9</sup>. Thermal reaction of pyrroles with dimethyl butinedioate can proceed by two different ways: a [4 + 2]cycloaddition, and Michael addition to the  $\alpha$  position of pyrrole. Formation of the cycloaddition products, or the ratio of both is determined by the character of the substituent at nitrogen atom and by reaction conditions<sup>4-6</sup>. 1,2-Dimethylindole gave with dimethyl butinedioate a product of Michael addition to position 3 (ref.<sup>7</sup>), 1-methylindole<sup>8</sup> and 2-ethoxy-1-methylindole<sup>9</sup> a substituted benzo[*b*]azepine; this indicated that this reaction proceeds as a [2 + 2]-cycloaddition.

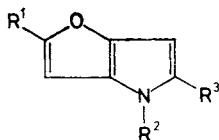
This paper concerns the reaction of 2-aryl-4H-furo[3,2-*b*]pyrrole<sup>3</sup> and its N-substituted analogues containing an electron-donating (CH<sub>3</sub>) and an electron-accepting (COCH<sub>3</sub>) substituent with dimethyl butinedioate in acetonitrile. 2-Phenyl-4H-furo[3,2-*b*]pyrrole and its N-methyl derivative gave products of Michael addition to position 5 - *IIIa,b*, 4-acetyl-2-arylfuro[3,2-*b*]pyrrole furnished a substituted benzo[*b*]furan. This result evidenced the transformation of pyrrole ring, nevertheless

the accessible spectral methods failed when determining the position of substituents at the benzene ring and therefore, neither the mechanism could be considered. We presumed this reaction to proceed either as a  $[4 + 2]$  cycloaddition typical of pyrrole derivatives (path *A*, Scheme 1), or, similarly as with indole derivatives, as a  $[2 + 2]$ -cycloaddition followed by a rearrangement of pyrrole ring to a seven-membered and further to a six-membered one (path *B*, Scheme 1).



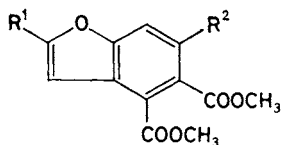
SCHEME 1

To determine the structure of the reaction product and to throw more light on the mechanism of rearrangement, the acetyl group was removed (compounds *Va,b*), the compound was diazotized and copulated to afford *VI*. This reaction proved involvement of the amino group bound to aromatic ring. Deamination under formation of *VII* showed, as evidenced by  $^1\text{H}$  NMR spectral data this compound to be 2-aryl-4,5-dimethoxycarbonylbenzo[*b*]furan and therefore, rearrangement of the pyrrole ring proceeded *via A*.

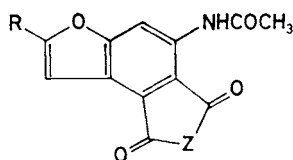


- I a*,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^2 = \text{COOCH}_3$ ;  $\text{R}^3 = \text{H}$   
*I b*,  $\text{R}^1 = 4\text{-CH}_3\text{-C}_6\text{H}_4$ ;  $\text{R}^2 = \text{COOCH}_3$ ;  $\text{R}^3 = \text{H}$   
*II a*,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^2 = \text{COOCH}_3$ ;  $\text{R}^3 = \text{COOC}_2\text{H}_5$   
*II b*,  $\text{R}^1 = 4\text{-CH}_3\text{-C}_6\text{H}_4$ ;  $\text{R}^2 = \text{COOCH}_3$ ;  $\text{R}^3 = \text{COOC}_2\text{H}_5$   
*III a*,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^2 = \text{H}$ ;  $\text{R}^3 = \text{C}(\text{COOCH}_3) = \text{CH}_A\text{COOCH}_3$   
*III b*,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^2 = \text{CH}_3$ ;  $\text{R}^3 = \text{C}(\text{COOCH}_3) = \text{CH}_A\text{COOCH}_3$

The presence of two carbonyl groups in neighbouring positions of 6-acetylamino-2-aryl-4,5-dimethoxycarbonylbenzo[*b*]furan was utilized for the reaction with hydrazine hydrate to cyclize the diazine ring (compounds *VIIIa,b*). Hydrolysis of the dimethoxycarbonyl groups led to a system containing a fused dihydrofuran ring to benzo[*b*]furan skeleton (compounds *IXa,b*); this fact indicates that the dicarboxylic acid formed passed into its anhydride.



- IV a*,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^2 = \text{NHCOCH}_3$   
*IV b*,  $\text{R}^1 = 4\text{-CH}_3\text{-C}_6\text{H}_4$ ;  $\text{R}^2 = \text{NHCOCH}_3$   
*V a*,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^2 = \text{NH}_2$   
*V b*,  $\text{R}^1 = 4\text{-CH}_3\text{-C}_6\text{H}_4$ ;  $\text{R}^2 = \text{NH}_2$   
*VI*,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^2 = \text{N}=\text{N-C}_6\text{H}_4\text{-OH}$   
*VII*,  $\text{R}^1 = \text{C}_6\text{H}_5$ ;  $\text{R}^2 = \text{H}$



- VIII a*,  $\text{R} = \text{C}_6\text{H}_5$ ;  $\text{Z} = \text{NH-NH}$   
*VIII b*,  $\text{R} = 4\text{-CH}_3\text{-C}_6\text{H}_4$ ;  $\text{Z} = \text{NH-NH}$   
*IX a*,  $\text{R} = \text{C}_6\text{H}_5$ ;  $\text{Z} = \text{O}$   
*IX b*,  $\text{R} = 4\text{-CH}_3\text{-C}_6\text{H}_4$ ;  $\text{Z} = \text{O}$

Compounds containing methoxycarbonyl groups attached to benzene ring *IV-VII* displayed in the IR spectrum one absorption ascribable to  $\nu(\text{CO})$  at 1715 to  $1718\text{ cm}^{-1}$ , compounds *IXa,b* two absorption bands typical of carbonyl groups

of acid anhydrides. The  $\nu(\text{CO})$  absorptions due to an acetyl group in compounds *I*, *II*, *IV*, *IX* lie at  $1\,685\text{--}1\,712\text{ cm}^{-1}$ . Electronic spectra of *Ia*, *b* reveal the most intense band at  $323\text{--}326\text{ nm}$ , corresponding to absorption of a furopyrrole condensed system<sup>3</sup>. Compounds *IIIa*, *b* have this band considerably bathochromically shifted to  $415\text{ nm}$  and  $432\text{ nm}$ , respectively, as a result of entering the multiple bond and carbonyl groups into conjugation with the heterocyclic ring. Spectra of compounds containing the benzofuran skeleton (*IV*–*VII*) have the most intense bands at  $250\text{ to }340\text{ nm}$ . The  $^1\text{H NMR}$  spectrum of *VII* shows three signals in the  $\text{H}_{\text{arom}}$  region associated with  $\text{C}_{(3)}\text{—H}$ ,  $\text{C}_{(6)}\text{—H}$  and  $\text{C}_{(7)}\text{—H}$ ; that of  $\text{C}_{(6)}\text{—H}$  is a doublet.  $\text{C}_{(7)}\text{—H}$  is a doublet ( $J_{6,7} = 8.5\text{ Hz}$ ).  $\text{C}_{(3)}$  and  $\text{C}_{(7)}$  are insignificantly split due to a long-range interaction ( $J_{3,7} = 0.7\text{ Hz}$ ).

## EXPERIMENTAL

### 4-Acetyl-2-phenylfuro[3,2-*b*]pyrrole (*Ia*)

2-Phenyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylic acid<sup>3</sup> (2.27 g, 10 mmol) was refluxed in acetic anhydride (30 ml) for 4 h. The solvent was distilled off and the raw product was crystallized. Yield 86%, m.p.  $112^\circ\text{C}$  (ethanol). For  $\text{C}_{14}\text{H}_{11}\text{NO}_2$  (225.3) calculated: 74.65% C, 4.92% H; 6.22% N; found: 74.42% C, 4.88% H, 6.20% N. IR spectrum ( $\text{CHCl}_3$ )  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1 702 ( $\text{C=O}$ ). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): 326 (3.22).  $^1\text{H NMR}$  spectrum ( $\text{C}^2\text{HCl}_3$ ,  $\delta$ , ppm): 7.45 (1 H, d,  $\text{C}_{(5)}\text{—H}$ ), 6.69 (1 H, d,  $\text{C}_{(3)}\text{—H}$ ), 6.33 (1 H, dd,  $\text{C}_{(6)}\text{—H}$ ), 2.53 (3 H, s,  $\text{CH}_3$ ), 2.53 (3 H, s,  $\text{CH}_3$ ), 7.20–7.75 (5 H, m,  $\text{H}_{\text{arom}}$ ),  $J_{5,6} = 3.7$ ,  $J_{3,6} = 0.8\text{ Hz}$ .

4-Acetyl-2-(4-tolyl)furo[3,2-*b*]pyrrole (*Ib*) was prepared in an analogous way. Yield 62%, m.p.  $142^\circ\text{C}$  (ethanol). For  $\text{C}_{15}\text{H}_{13}\text{NO}_3$  (239.1) calculated: 75.28% C, 5.48% H, 5.91% N; found: 75.18% C, 5.46% H, 5.86% N. IR spectrum ( $\text{CHCl}_3$ )  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1 692 ( $\text{C=O}$ ). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2\text{ mol}^{-1}$ ): 323 (3.20).  $^1\text{H NMR}$  spectrum ( $\text{C}^2\text{HCl}_3$ ,  $\delta$ , ppm): 7.17 (1 H, d,  $\text{C}_{(5)}\text{—H}$ ), 6.85 (1 H, d,  $\text{C}_{(3)}\text{—H}$ ), 6.29 (1 H, dd,  $\text{C}_{(6)}\text{—H}$ ), 2.52 (3 H, s,  $\text{CH}_3$ ), 2.34 (3 H, s,  $\text{CH}_3$ ), 7.12, 7.55 (4 H, dd,  $\text{H}_{\text{arom}}$ ),  $J_{5,6} = 3.7$ ,  $J_{3,6} = 0.8\text{ Hz}$ .

Ethyl 4-acetyl-2-phenylfuro[3,2-*b*]pyrrole-5-carboxylate (*IIa*) was obtained by a 8-h reflux. Yield 79%, m.p.  $93^\circ\text{C}$  (ethanol). For  $\text{C}_{17}\text{H}_{15}\text{NO}_4$  (297.3) calculated: 68.68% C, 5.08% H, 4.71% N; found: 68.42% C, 4.96% H, 4.43% N. IR spectrum (KBr)  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1 702 ( $\text{C=O}$ ). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2\text{ mol}^{-1}$ ): 352 (3.27).  $^1\text{H NMR}$  spectrum ( $\text{C}^2\text{HCl}_3$ ,  $\delta$ , ppm): 7.00 (1 H, d,  $\text{C}_{(3)}\text{—H}$ ), 7.00 (1 H, d,  $\text{C}_{(6)}\text{—H}$ ), 4.33 (2 H, q,  $\text{CH}_2$ ), 2.66 (3 H, s,  $\text{CH}_3$ ), 1.37 (3 H, t,  $\text{CH}_3$ ), 7.81–7.27 (5 H, m,  $\text{H}_{\text{arom}}$ ),  $J_{3,6} = 0.8\text{ Hz}$ .

Ethyl 4-acetyl-2-(4-tolyl)furo[3,2-*b*]pyrrole-5-carboxylate (*IIb*) was prepared as *IIa*. Yield 74%, m.p.  $116^\circ\text{C}$  (ethanol). For  $\text{C}_{18}\text{H}_{17}\text{NO}_4$  (311.3) calculated: 69.44% C, 5.50% H, 4.49% N; found: 69.11% C, 5.39% H, 4.28% N. IR spectrum (KBr)  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1 700 ( $\text{C=O}$ ). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2\text{ mol}^{-1}$ ): 354 (3.44).  $^1\text{H NMR}$  spectrum ( $\text{C}^2\text{HCl}_3$ ,  $\delta$ , ppm): 6.97 (1 H, d,  $\text{C}_{(6)}\text{—H}$ ), 6.65 (1 H, d,  $\text{C}_{(3)}\text{—H}$ ), 4.32 (2 H, q,  $\text{CH}_2$ ), 2.66 (3 H, s,  $\text{CH}_3$ ), 2.36 (3 H, s,  $\text{CH}_3$ ), 1.37 (3 H, t,  $\text{CH}_3$ ), 7.60, 7.17 (4 H, dd,  $\text{H}_{\text{arom}}$ ),  $J_{3,6} = 0.8\text{ Hz}$ .

### Dimethyl 2-Phenyl-4*H*-furo[3,2-*b*]-5-pyrrolylbutenedioate (*IIIa*)

A mixture of 2-phenyl-4*H*-furo[3,2-*b*]pyrrole<sup>3</sup> (1.8 g, 10 mmol) and dimethyl butenedioate (1.4 g,

10 mmol) in acetonitrile (10 ml) was left to stand in the dark for 24 h. The precipitated orange compound was filtered off. Yield 31%, m.p. 124°C (ethanol). For  $C_{18}H_{15}NO_5$  (325.5) calculated: 66.52% C, 4.65% H, 4.31% N; found: 66.31% C, 4.43% H, 4.12% N. IR spectrum (KBr)  $\tilde{\nu}_{\max}$ ,  $cm^{-1}$ : 1 712 (C=O), 1 664 (C=O). UV spectrum  $\lambda_{\max}$ , nm ( $\log \epsilon$ ,  $m^2 \text{ mol}^{-1}$ ): 432 (3.42).  $^1H$  NMR spectrum ( $C^2HCl_3$ ,  $\delta$ , ppm): 6.69 (1 H, d,  $C_{(3)}-H$ ), 6.58 (1 H, dd,  $C_{(6)}-H$ ), 5.93 (1 H, s,  $H_A$ ), 3.90 (3 H, s,  $CH_3$ ), 3.79 (3 H, s,  $CH_3$ ), 7.78–7.22 (5 H, m,  $H_{\text{arom}}$ ),  $J_{3,6} = 0.8$  Hz.

*Dimethyl 2-phenyl-4-methoxyfuro[3,2-*b*]-5-pyrrolylbutenedioate* (IIIb) was synthesized analogically. Yield 27%, m.p. 164°C (ethanol). For  $C_{19}H_{17}NO_5$  (339.3) calculated: 67.25% C, 5.05% H, 4.13% N; found: 66.82% C, 4.97% H, 4.03% N. IR spectrum (KBr)  $\tilde{\nu}_{\max}$ ,  $cm^{-1}$ : 1 735 (C=O), 1 699 (C=O). UV spectrum  $\lambda_{\max}$ , nm ( $\log \epsilon$ ,  $m^2 \text{ mol}^{-1}$ ): 415 (3.53).  $^1H$  NMR spectrum ( $C^2HCl_3$ ,  $\delta$ , ppm): 6.67 (1 H, d,  $C_{(3)}-H$ ), 6.33 (1 H, d,  $C_{(6)}-H$ ), 5.98 (1 H, s,  $H_A$ ), 4.85 (3 H, s,  $CH_3$ ), 3.78, 3.76 (3 H, s,  $CH_3$ ), 7.65–7.25 (5 H, m,  $H_{\text{arom}}$ ),  $J_{3,6} = 0.8$  Hz.

#### 6-Acetylamido-2-phenyl-4,5-dimethoxycarbonylbenzo[*b*]furan (*IVa*)

A mixture of *Ia* (2.1 g, 10 mmol) and dimethyl butinedioate (2 g, 14 mmol) was refluxed in acetonitrile for 6 days. The precipitated substance was filtered off. Yield 56%, m.p. 197°C (ethanol). For  $C_{20}H_{17}NO_6$  (367.3) calculated: 65.39% C, 4.66% H, 3.81% N; found: 64.96% C, 4.49% H, 3.67% N. IR spectrum (KBr)  $\tilde{\nu}_{\max}$ ,  $cm^{-1}$ : 1 716 (C=O), 1 698 (C=O). UV spectrum  $\lambda_{\max}$ , nm ( $\log \epsilon$ ,  $m^2 \text{ mol}^{-1}$ ): 432 (3.36), 302 (3.25), 256 (3.42).  $^1H$  NMR spectrum ( $C^2HCl_3$ ,  $\delta$ , ppm): 9.40 (1 H, bs, NH), 8.70 (1 H, d,  $C_{(7)}-H$ ), 7.11 (1 H, d,  $C_{(3)}-H$ ), 3.90 (6 H, s, 2  $CH_3$ ), 2.21 (3 H, s,  $CH_3$ ), 7.87–7.25 (5 H, m,  $H_{\text{arom}}$ ). Mass spectrum,  $m/z$  (relat. intens., %): 367 (100), 325 (80), 293 (36), 235 (24), 207 (68).

*6-Acetylamido-2-(4-tolyl)-4,5-dimethoxycarbonylbenzo[*b*]furan* (*IVb*) was prepared in the same way. Yield 52%, m.p. 192°C (ethanol). For  $C_{21}H_{19}NO_6$  (381.4) calculated: 66.13% C, 5.0% H, 3.67% N; found: 65.92% C, 5.22% H, 3.47% N. IR spectrum (KBr)  $\tilde{\nu}_{\max}$ ,  $cm^{-1}$ : 1 716 (C=O), 1 712 (C=O). UV spectrum  $\lambda_{\max}$ , nm ( $\log \epsilon$ ,  $m^2 \text{ mol}^{-1}$ ): 436 (3.20), 303 (3.07), 260 (3.23).  $^1H$  NMR spectrum ( $C^2HCl_3$ ,  $\delta$ , ppm): 9.48 (1 H, bs, NH), 8.60 (1 H, d,  $C_{(7)}-H$ ), 7.03 (1 H, s,  $C_{(3)}-H$ ), 3.88 (6 H, s, 2  $CH_3$ ), 2.35 (1 H, s,  $CH_3$ ), 2.18 (3 H, s,  $CH_3$ ), 7.06, 7.16 (4 H, dd,  $H_{\text{arom}}$ ).

#### 6-Amino-2-phenyl-4,5-dimethoxycarbonylbenzo[*b*]furan (*Va*)

Compound *IVa* (3.67 g, 10 mmol) dissolved in methanol (c. 250 ml) was refluxed with dilute (1 : 1) hydrochloric acid (10 ml) for 4 h. The mixture was cooled and the precipitated compound was filtered off. Yield 98%, m.p. 133°C (methanol). For  $C_{18}H_{15}NO_5$  (325.3) calculated: 66.52% C, 4.65% H, 4.31% N; found: 66.18% C, 4.28% H, 4.25% N. IR spectrum (KBr)  $\tilde{\nu}_{\max}$ ,  $cm^{-1}$ : 1 718 (C=O). UV spectrum  $\lambda_{\max}$ , nm ( $\log \epsilon$ ,  $m^2 \text{ mol}^{-1}$ ): 381 (3.25), 307 (3.25), 264 (3.37).  $^1H$  NMR spectrum ( $CF_3COO^2H$ ,  $\delta$ , ppm): 7.56 (1 H, d,  $C_{(7)}-H$ ), 6.78 (1 H, d,  $C_{(3)}-H$ ), 3.76 (3 H, s,  $CH_3$ ), 3.67 (3 H, s,  $CH_3$ ), 7.60–6.98 (5 H, m,  $H_{\text{arom}}$ ),  $J_{3,7} = 0.7$  Hz. Mass spectrum  $m/z$  (relat. intens., %): 325 (100), 293 (32), 279 (14), 235 (28), 207 (82), 103.5 (14).

*6-Amino-2-(4-tolyl)-4,5-dimethoxycarbonylbenzo[*b*]furan* (*Vb*) was obtained by the same procedure. Yield 98%, m.p. 144°C (methanol). For  $C_{19}H_{17}NO_5$  (339.4) calculated: 67.25% C, 5.05% H, 4.13% N; found: 67.11% C, 4.97% H, 3.99% N. IR spectrum (KBr)  $\tilde{\nu}_{\max}$ ,  $cm^{-1}$ : 1 715 (C=O). UV spectrum  $\lambda_{\max}$ , nm ( $\log \epsilon$ ,  $m^2 \text{ mol}^{-1}$ ): 383 (3.34), 310 (3.41), 267 (3.48).  $^1H$  NMR spectrum ( $CF_3COO^2H$ ,  $\delta$ , ppm): 7.75 (1 H, d,  $C_{(7)}-H$ ), 7.12 (1 H, d,  $C_{(3)}-H$ ), 4.18 (3 H, s,  $CH_3$ ), 4.11 (3 H, s,  $CH_3$ ), 7.64, 7.31 (4 H, dd,  $H_{\text{arom}}$ ),  $J_{3,7} = 0.7$  Hz.

## 2-Phenyl-6-(4-hydroxyphenyl)azo-4,5-dimethoxycarbonyl[b]furan (VI)

To a stirred *Va* (3.25 g, 10 mmol) in dilute hydrochloric acid (20 ml) sodium nitrite (0.4 g) in water (10 ml) was added at  $-5^{\circ}\text{C}$ . Phenol (0.9 g, 10 mmol) in water (10 ml) was added to the diazotized compound and the red precipitate was filtered off. Yield 47%, m.p.  $267^{\circ}\text{C}$  (ethanol). For  $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_6$  (430.3) calculated: 66.99% C, 4.18% H, 6.51% N; found: 65.48% C, 3.89% H, 6.39% N. IR spectrum (KBr)  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1715 (C=O), 1591 (N=N). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2 \text{mol}^{-1}$ ): 410 (3.53), 345 (3.54), 257 (3.42).  $^1\text{H}$  NMR spectrum (hexadeuteriodimethyl sulfoxide,  $\delta$ , ppm): 8.10 (1 H, d,  $\text{C}_{(7)}\text{-H}$ ), 7.65 (1 H, d,  $\text{C}_{(3)}\text{-H}$ ), 8.12–7.42 (5 H, m,  $\text{H}_{\text{arom}}$ ), 7.71, 6.93 (4 H, dd,  $\text{H}_{\text{arom}}$ ),  $J_{3,7} = 0.7$  Hz.

## 2-Phenyl-4,5-dimethoxycarbonylbenzo[b]furan (VII)

A solution of *VI* (3.25 g, 10 mmol) in dimethylformamide (14 ml) was added to a stirred solution of pentylnitride (1.2 g, 15 mmol) in dimethylformamide (6 ml) at  $50^{\circ}\text{C}$ . The mixture was stirred for additional 30 min, poured into water and the product was taken with ether. The combined ethereal extracts were washed with water, dried with sodium sulfate, the solvent was removed and the raw product was crystallized. Yield 87%, m.p.  $97^{\circ}\text{C}$  (ethanol). For  $\text{C}_{18}\text{H}_{14}\text{O}_5$  (310.3) calculated: 69.67% C, 4.55% H; found: 69.43% C, 4.38% H. IR spectrum (KBr)  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1718 (C=O). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2 \text{mol}^{-1}$ ): 331 (3.27), 301 (3.19), 290 (3.19), 260 (3.26).  $^1\text{H}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ,  $\delta$ , ppm): 7.71 (1 H, d,  $\text{C}_{(6)}\text{-H}$ ), 7.61 (1 H, dd,  $\text{C}_{(7)}\text{-H}$ ), 7.22 (1 H, d,  $\text{C}_{(3)}\text{-H}$ ), 4.00 (3 H, s,  $\text{CH}_3$ ), 3.92 (3 H, s,  $\text{CH}_3$ ), 7.91–7.33 (5 H, n,  $\text{H}_{\text{arom}}$ ),  $J_{3,7} = 0.7$  Hz,  $J_{6,7} = 8.5$  Hz.

8-Acetylamido-2-phenyl-4,5,6,7-tetrahydrobenzo[b]furo-[4,5-*d*]pyridazine-4,7-dione (VIIIa)

Compound *IVa* (3.67 g, 10 mmol) was refluxed with hydrazine hydrate (1 g, 60 mmol) in ethanol for 3 days. The precipitated compound was filtered off. Yield 87%, m.p.  $301^{\circ}\text{C}$  (dimethylformamide). For  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}_4$  (355.3) calculated: 67.47% C, 3.90% H, 12.53% N; found: 64.23% C, 3.79% H, 12.46% N. IR spectrum (KBr)  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1645 (C=O), 1641 (C=O). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2 \text{mol}^{-1}$ ): 383 (3.33), 368 (3.34), 342 (3.28).  $^1\text{H}$  NMR spectrum (hexadeuteriodimethyl sulfoxide): 9.00 (1 H, bs, NH), 7.72 (1 H, d,  $\text{C}_{(9)}\text{-H}$ ), 7.38 (1 H, d,  $\text{C}_{(3)}\text{-H}$ ), 2.13, (3 H, s,  $\text{CH}_3$ ), 7.95–7.40 (5 H, m,  $\text{H}_{\text{arom}}$ ).

8-Acetylamido-2-(4-tolyl)-4,5,6,7-tetrahydrobenzo[b]furo[4,5-*d*]pyridazine-4,7-dione (VIIIb) obtained analogously in a 84% yield. M.p.  $274^{\circ}\text{C}$  (dimethylformamide). For  $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_4$  (369.4) calculated: 65.32% C, 4.33% H, 12.03% N; found: 64.92% C, 4.27% H, 11.89% N. IR spectrum (KBr)  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1646 (C=O), 1640 (C=O). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2 \text{mol}^{-1}$ ): 384 (3.23), 363 (3.39), 343 (3.36).  $^1\text{H}$  NMR spectrum (hexadeuteriodimethyl sulfoxide): 9.10 (1 H, bs, NH), 7.79 (1 H, d,  $\text{C}_{(9)}\text{-H}$ ), 7.37 (1 H, d,  $\text{C}_{(3)}\text{-H}$ ), 2.37 (3 H, s,  $\text{CH}_3$ ), 2.20 (3 H, s,  $\text{CH}_3$ ), 7.31, 7.75 (4 H, dd,  $\text{H}_{\text{arom}}$ ).

7-Acetylamido-4,6-dihydro-2-phenylfuro[3,4-*e*]benzo[b]furan-4,6-dione (IXa)

To a solution of *IVa* (3.67 g, 10 mmol) in ethanol (250 ml) 5%-NaOH (60 ml) was added and the mixture was refluxed for 2 h. The solvent was removed and the precipitated salt was dissolved in ethanol-water (1 : 1) and hot-precipitated with dilute hydrochloric acid. The precipitate was filtered off. Yield 71%, m.p.  $283^{\circ}\text{C}$  (dimethylformamide). For  $\text{C}_{18}\text{H}_{11}\text{NO}_5$  (321.3) calculated: 67.29% C, 3.45% H, 4.35% N; found: 67.13% C, 3.32% H, 4.17% N. IR spectrum (KBr)  $\tilde{\nu}_{\text{max}}$ ,

$\text{cm}^{-1}$ : 1 824 (C=O), 1 739 (C=O), 1 685 (C=O). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2 \text{mol}^{-1}$ ): 406 (3·28), 367 (3·42), 288 (3·62). Mass spectrum,  $m/z$  (relat. intens., %): 321 (39), 279 (100), 207 (68), 77 (9·6), 43 (32), 28 (19).

7-Acetylamido-4,6-dihydro-2-(4-tolyl)furo[3,4-*e*]benzo[*b*]furan-4,6-dione (IXb). Yield 67%, m.p. 293°C (dimethylformamide). For  $\text{C}_{19}\text{H}_{13}\text{NO}_5$  (335·3) calculated: 68·06% C, 3·91% H, 4·02% N; found: 67·79% C, 3·69% H, 4·12% N. IR spectrum (KBr)  $\tilde{\nu}_{\text{max}}$ ,  $\text{cm}^{-1}$ : 1 826 (C=O), 1 751 (C=O), 1 710 (C=O). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{m}^2 \text{mol}^{-1}$ ): 408 (3·27), 321 (3·42), 291 (3·51).

#### Spectral Measurements

Infrared spectra were measured with a Specord 71 IR (Zeiss, Jena) spectrophotometer, the electronic spectra with a Specord UV VIS (Zeiss, Jena) apparatus at a  $1 \cdot 10^{-5}$ – $5 \cdot 10^{-5} \text{ mol l}^{-1}$  concentration. Spectra of I–IV refer to methanolic solutions, those of V–IX to dioxane solutions. The  $^1\text{H}$  NMR spectra were recorded with a Tesla BS 487 C apparatus operating at 80 MHz; tetramethylsilane was the internal reference for measurements in  $\text{C}^2\text{HCl}_3$  and  $\text{CF}_3\text{COO}^2\text{H}$ , and hexamethyldisiloxane for those in hexadeuteriodimethyl sulfoxide.

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