

## THE SYNTHESIS AND REACTIONS OF ARYLFUROCONDENSED DERIVATIVES\*

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The preparation of new 9-arylfuro[2',3':4,5]pyrrolo[1,2-*d*]-1,2,4-triazolo[3,4-*f*]-1,2,4-triazines (*V*) and 7-aryl-1,4-dioxo-1,2,3,4-tetrahydrofuro[2',3':4,5]pyrrolo[1,2-*d*]-1,2,4-triazines (*VII*) from 2-aryl-4*H*-furo[3,2-*b*]pyrrole-5-carbohydrazides (*I*) is described. Reaction of *I* with triethyl orthoformate or acetate afforded 7-aryl-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-*d*]-1,2,4-triazin-1-ones, or their 4-methyl analogues *II* giving with phosphorus pentasulfide thiones *III*, reacting with hydrazine to the corresponding hydrazides *IV*. Cyclization of *IV* with orthoformates, or orthoacetates led to *V*. Methylchloro formate reacted with *I* to yield N-methoxycarbonyl-2-aryl-4*H*-furo[3,2-*b*]pyrrole-5-carbohydrazides *VI* undergoing cyclization in an alkaline medium to *VII*.

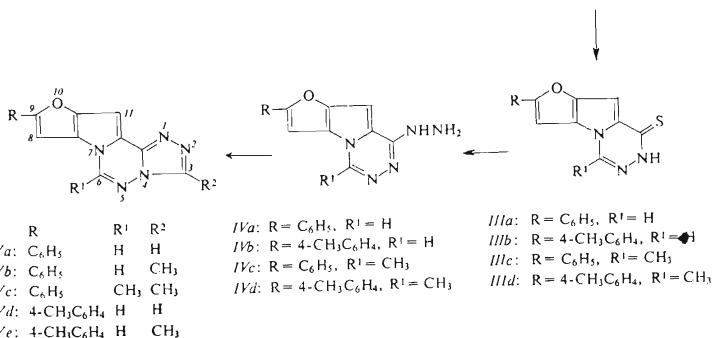
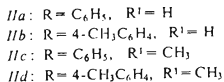
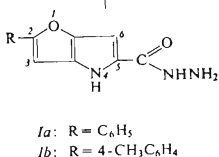
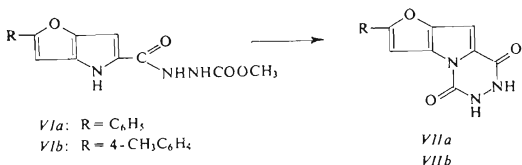
The synthesis of some condensation products derived from triazole<sup>1-4</sup> or triazine<sup>5-9</sup> was of special interest in the last few years. Some of the just mentioned products are biologically effective<sup>10,11</sup>. Ethyl 2-aryl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylatès, the preparation of which was the subject of our preceding papers<sup>12,13</sup>, were now reacted with hydrazine to form hydrazides *I*.

Two reaction centres of 2-aryl-4*H*-furo[3,2-*b*]pyrrole-5-carbohydrazides were employed in a cyclization reaction with triethyl orthoformate and orthoacetate leading to 7-arylfuro[2',3':4,5]pyrrolo[1,2-*d*]-1,2,4-triazin-1-ones (*II*). Compounds *IIa*–*IId* (Scheme 1) afforded with phosphorus sulfide thiones *III*, pyridine being the suitable solvent. The successful reaction course was subject to a high purity of the solvent, high concentration of both reactants and a vigorous stirring.

7-Arylfuro[2',3':4,5]pyrrolo[1,2-*d*]-1,2,4-triazine-1-thiones yield with hydrazine hydrate 7-aryl-1-hydrazino[2',3':4,5]pyrrolo[1,2-*d*]1,2,4-triazines *IV* having anew two reaction centres. Reaction with triethyl orthoformate, or orthoacetate gave 9-arylfuro[2',3':4,5]pyrrolo[1,2-*d*]-1,2,4-triazolo[3,4-*f*]1,2,4-triazines and 3- and 6-methyl, as well as 3,6-dimethyl derivatives, respectively. The last reaction requires a water-free reaction medium, the suitable solvent being dimethylformamide.

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N-Methoxycarbonylhydrazides *VI* were prepared by treatment of 2-aryl-4H-furo[3,2-b]pyrrole-5-carbohydrazides with methyl chloroformate. The not arylated hydrazide furnished a tarry product; this fact can be rationalized by a lower stability of the starting system towards hydrogen chloride freed during reaction. An alkaline hydrolysis of *VIa,b* afforded 7-aryl-1,4-dioxo-1,2,3,4-tetrahydrofuro[2',3'-4,5]pyrrolo[1,2-d]1,2,4-triazines *VII*.



SCHEME 1

The IR spectra of *Va* – *Ve* showed absorption bands of C=N vibrations of triazole and triazine rings at 1 630 and 1 580  $\text{cm}^{-1}$ , the band at the lower wave number being more intense. Bands of the same wavelengths were also found in spectra of compounds *IV*. These revealed  $\nu(\text{C—H})$  at 2 963–2 995  $\text{cm}^{-1}$  and  $\nu(\text{C—H})$  arom at 3 300–3 060  $\text{cm}^{-1}$ . Wave numbers of N—H bonds in the spectra of compounds taken in KBr were at 3 350–3 160  $\text{cm}^{-1}$ .

Compounds *VIIa,b* exist, in relation to the medium, in two tautomeric forms; their IR spectra in KBr displayed absorption bands belonging to (C=O) indicating the lactam form, the  $^1\text{H}$  NMR spectra do not show signals of NH groups in hexa-deuteriodimethyl sulfoxide. A similar feature was observed<sup>14</sup> with 1,4-dioxo-1,2,3,4-tetrahydropyrrolo[1,2-*d*]-1,2,4-triazine.

The electronic spectra of all mentioned compounds were characteristic of an intense absorption band ( $\log \epsilon = 4.36$ – $4.83$ ) in the 313–340 nm range and a series of weaker bands at 200–300 nm, corresponding to  $\pi \rightarrow \pi^*$  electronic transitions. Relatively high values  $\lambda_{\text{max}}$  344–349 nm were found, as expected, with compounds *V*, having four fused rings. Spectra of compounds *III* and *IV* were measured in methanol both in neutral and acidic medium. The changes in  $\lambda_{\text{max}}$  and in band intensities evidence tautomerism of these compounds.

Protons of the furopyrrole grouping ( $\text{H}_3$ ,  $\text{H}_6$ ,  $\text{H}_6$ ,  $\text{H}_9$ , or  $\text{C}_6$ ,  $\text{H}_{11}$ ) have a little lower chemical shift values with 4-tolyl substitution than those with a phenyl substitution, due to an electron donating character of the 4-tolyl group. Long-range coupling constant between these protons in all compounds investigated was found to be  $J = 0.8$  Hz. Formation of 1,2,4-triazine derivatives *IIa*–*IId* was backed by the  $\text{C}_{(6)}\text{—H}$ , or  $\text{C}_{(6)}\text{—CH}_3$  proton signal, and from the change in multiplicity of the  $\text{C}_{(9)}\text{—H}$  proton signal from the doublet-doublet to a doublet. Replacement of oxygen in *II* by sulfur in substance *III* results in a downfield shift of furopyrrole  $\text{C}_{(6)}\text{—H}$ ,  $\text{C}_{(9)}\text{—H}$  proton signals by 0.1 ppm; the  $\text{C}_{(6)}\text{—H}$  and  $\text{C}_{(9)}\text{—H}$  proton chemical shift values of compounds *IV* were shifted by 0.3 and 0.5 ppm, respectively. The structure of compounds *V* was corroborated by the presence of  $\text{C}_{(3)}\text{—H}$ , or  $\text{C}_{(3)}\text{—CH}_3$  proton signals analogously as reported<sup>10,15</sup>.

## EXPERIMENTAL

### 2-Phenyl-3*H*-furo[3,2-*b*]pyrrole-5-carboxylate (*Ia*)

80% Hydrazine hydrate (3.5 g) was added to a solution of ethyl 2-phenyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (1 g, 4 mmol) in ethanol (50 ml), the mixture was refluxed for 40 h and the separated crystals were filtered off after cooling; yield 0.83 g (89%), m.p. 232°C (ethanol). For  $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$  (241.3) calculated: 64.70% C, 4.59% H, 17.42% N; found: 64.52% C, 5.49% H, 17.31% H. IR spectrum,  $\text{cm}^{-1}$ : 1 614 (C=O). UV spectrum  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ): 333 (3.47), 279 (3.24).  $^1\text{H}$  NMR spectrum: 7.09 (1 H, d,  $\text{C}_{(3)}\text{—H}$ ), 6.85 (1 H,  $\text{C}_{(6)}\text{—H}$ ), 7.25–7.93 (5 H, m,  $\text{H}_{\text{arom}}$ ,  $J_{3,6} = 0.8$ ).

2-(4-Tolyl)-4H-furo[3,2-b]pyrrole-5-carbohydrazide (Ib) was obtained analogously. Yield 84%, m.p. 257°C (ethanol). For  $C_{14}H_{13}N_3O_2$  (255.3) calculated: 65.85% C, 5.13% H, 16.16% N, found: 65.76% C, 5.06% H, 16.31% N, IR spectrum,  $cm^{-1}$ : 1 623 (C=O). UV spectrum,  $\lambda_{max}$ , nm. (log  $\epsilon$ ): 342 (3.77), 211 (3.11).  $^1H$  NMR spectrum: 6.98 (1 H, d,  $C_{(3)}$ -H), 6.81 (1 H, dd,  $C_{(6)}$ -H), 7.65, 7.21 (4 H, d,  $H_{arom}$ ,  $J_{3,6} = 0.8$ ).

7-Phenyl-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazin-1-one (IIa)

Ester Ia (2.65 g, 11 mmol) and triethyl orthoformate (2 g, 12 mmol) in dimethylformamide (10 ml) were refluxed for 2.5 h and the crystals after cooling were filtered off. Yield 2.18 g (79%), m.p. 312°C (dimethylformamide). For  $C_{14}H_9N_3O_2$  (251.2) calculated: 66.93% C, 3.61% H, 16.72% N; found: 66.88% C, 3.59% H, 16.71% N. IR spectrum,  $cm^{-1}$ : 1 656 (C=O). UV spectrum,  $\lambda_{max}$ , nm (log  $\epsilon$ ): 333 (3.64), 279 (3.23).  $^1H$  NMR spectrum: 7.16 (1 H, d,  $C_{(6)}$ -H), 7.41 (1 H, d,  $C_{(9)}$ -H), 8.71 (1 H, s,  $C_{(4)}$ -H), 7.25–7.87 (5 H, m,  $H_{arom}$ ,  $J_{6,9} = 0.8$  Hz).

7-(4-Tolyl)-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazin-1-one (II) was prepared in the same way. Yield 78%, m.p. 347°C (dimethylformamide). For  $C_{15}H_{11}N_3O_2$  (265.3) calculated: 71.71% C, 4.18% H, 15.84% N; found: 71.80% C, 4.18% H, 15.84% N. IR spectrum,  $cm^{-1}$ : 1 657 (C=O), UV spectrum,  $\lambda_{max}$ , nm. (log  $\epsilon$ ): 335 (3.60), 227 (3.27).  $^1H$  NMR spectrum: 7.04 (1 H, d,  $C_{(6)}$ -H), 7.37 (1 H, d,  $C_{(9)}$ -H), 8.56 (1 H, s,  $C_{(4)}$ -H), 7.29, 7.79 (4 H, d,  $H_{arom}$ ),  $J_{6,9} = 0.8$  Hz.

4-Methyl-7-(4-tolyl)-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-d]1,2,4-triazin-1-one (IIId) was synthesized from Id. Yield 80%, m.p. 348°C (dimethylformamide). For  $C_{16}H_{13}N_3O_2$  (279.3) calculated: 68.80% C, 4.69% H, 15.04% N; found: 68.76% C, 4.59% H, 15.18% N. IR spectrum  $cm^{-1}$ : 1 641 (C=O). UV spectrum,  $\lambda_{max}$ , nm (log  $\epsilon$ ): 320 (3.52), 205 (2.90).  $^1H$  NMR spectrum: 7.09 (1 H, d,  $C_{(6)}$ -H), 7.57 (1 H, d,  $C_{(9)}$ -H), 7.22, 7.69 (4 H, d,  $H_{arom}$ ), 2.64 (3 H, s,  $C_{(5)}$ -CH<sub>3</sub>),  $J_{6,9} = 0.8$  Hz.

7-Phenyl-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine-1-thione (IIIa)

A mixture of IIa (2.51 g, 10 mmol) and phosphorus pentasulfide (2 g, 9 mmol) was refluxed in pyridine (10 ml) for 4 h while stirred, and poured into hot water (30 ml). The separated precipitate was filtered off; yield 1.84 g (69%), m.p. 328°C (dioxane). For  $C_{14}H_9N_3OS$  (268.1) calculated: 62.71% C, 3.38% H, 15.67% N, 11.96% S; found: 62.66% C, 3.42% H, 14.70% N, 11.86% S. IR spectrum,  $cm^{-1}$ : 1 537 (C=S). UV spectrum,  $\lambda_{max}$ , nm. (log  $\epsilon$ ): 335 (3.50), 400 (3.01).  $^1H$  NMR spectrum: 7.23 (1 H, d,  $C_{(6)}$ -H), 7.59 (1 H, d,  $C_{(9)}$ -H), 9.07 (1 H, s,  $C_{(4)}$ -H), 7.40–7.87 (5 H, m,  $H_{arom}$ ).

Following substances were obtained in an analogous way:

7-(4-Tolyl)-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine-1-thione (IIIb). Yield 71%, m.p. 313°C (dioxane). For  $C_{15}H_{11}N_3OS$  (282.2) calculated: 63.83% C, 3.93% H, 14.89% N, 11.36% S; found: 63.76% C, 3.95% H, 14.51% N, 11.32% S. IR spectrum,  $cm^{-1}$ : 1 537 (C=S). UV spectrum,  $\lambda_{max}$ , nm (log  $\epsilon$ ): 313 (3.07), 400 (3.05).  $^1H$  NMR spectrum: 7.24 (1 H, d,  $C_{(6)}$ -H), 7.49 (1 H, d,  $C_{(9)}$ -H), 9.03 (1 H, d,  $C_{(4)}$ -H), 7.25, 7.49 (4 H, d,  $H_{arom}$ ), 2.29 (3 H, s,  $C_{arom}$ -CH<sub>3</sub>).

7-Phenyl-4-methyl-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine-1-thione (IIIc). Yield 65%, m.p. 310°C (dioxane). For  $C_{15}H_{11}N_3OS$  (282.2) calculated: 63.83% C, 3.93% H, 14.89% N, 11.36% S; found: 63.58% C, 3.90% H, 14.48% N, 11.28% S. IR spectrum,  $cm^{-1}$ : 1 537 (C=S).



UV spectrum,  $\lambda_{\max}$ , nm, (log  $\epsilon$ ): 335 (31.6), 400 (3.01).  $^1\text{H}$  NMR spectrum: 7.23 (1 H, d,  $\text{C}_{(6)}\text{—H}$ ), 7.59 (1 H, d,  $\text{C}_{(9)}\text{—H}$ ), 7.38—7.88 (5 H, m,  $\text{H}_{\text{arom}}$ ), 2.69 (3 H, s,  $\text{C}_{(5)}\text{—CH}_3$ ).

4-Methyl-7-(4-tolyl)-1,2-dihydrofuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine-1-thione (IIIId). Yield 67%, m.p. 350°C (dioxane). For  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{OS}$  (296.2) calculated: 64.88% C, 4.42% H, 14.18% N, 10.82% S; found: 64.72% C, 4.60% H, 14.48% N, 10.90% S. IR spectrum,  $\text{cm}^{-1}$ : 1537 (C=S), UV spectrum,  $\lambda_{\max}$ , nm, (log  $\epsilon$ ): 312 (31.6), 400 (3.13).  $^1\text{H}$  NMR spectrum: 7.23 (1 H, d,  $\text{C}_{(6)}\text{—H}$ ), 7.64 (1 H, d,  $\text{C}_{(9)}\text{—H}$ ), 7.34, 7.64 (4 H, d,  $\text{H}_{\text{arom}}$ ), 3.07 (3 H, s,  $\text{C}_{(5)}\text{—CH}_3$ ), 2.45 (3 H, s,  $\text{C}_{\text{arom}}\text{—CH}_3$ ).

#### 7-Phenyl-1-hydrazinofuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine (IVa)

Compound IIIa (2.68 g, 10 mmol) and 94% hydrazine hydrate (15 ml) were heated at 80°C for 6 h, cooled, the separated substance filtered off and washed with ether. Yield 2.12 g (79%), m.p. 281°C (dioxane). For  $\text{C}_{14}\text{H}_{11}\text{N}_5\text{O}$  (268.3) calculated: 62.66% C, 4.13% H, 26.10% N; found: 62.46% C, 4.10% H, 26.30% N. UV spectrum,  $\lambda_{\max}$ , nm, (log  $\epsilon$ ): 354 (3.59).  $^1\text{H}$  NMR spectrum: 6.94 (1 H, d,  $\text{C}_{(6)}\text{—H}$ ), 7.07 (1 H, d,  $\text{C}_{(9)}\text{—H}$ ), 8.37 (1 H, s,  $\text{C}_{(4)}\text{—H}$ ), 7.29—7.80 (5 H, m,  $\text{H}_{\text{arom}}$ ),  $J_{6,9} = 0.8$  Hz.

Analogously were prepared:

1-Hydrazino-7-(4-tolyl)furo[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine (IVb). Yield 81%, m.p. 314°C (dioxane). For  $\text{C}_{15}\text{H}_{13}\text{N}_5\text{O}$  (279.3) calculated: 64.50% C, 4.69% H, 25.07% N; found: 64.48% C, 4.52% H, 24.77% N. UV spectrum,  $\lambda_{\max}$ , nm, (log  $\epsilon$ ): 349 (3.56).  $^1\text{H}$  NMR spectrum: 6.91 (1 H, d,  $\text{C}_{(6)}\text{—H}$ ), 6.96 (1 H, d,  $\text{C}_{(9)}\text{—H}$ ), 8.34 (1 H, s,  $\text{C}_{(4)}\text{—H}$ ), 7.63, 7.19 (4 H, d,  $\text{H}_{\text{arom}}$ ),  $J_{6,9} = 0.8$  Hz).

7-Phenyl-1-hydrazino-4-methylfuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine (IVc). Yield 92%, m.p. 328°C (dioxane). For  $\text{C}_{15}\text{H}_{13}\text{N}_5\text{O}$  (279.3) calculated: 64.50% C, 4.69% H, 25.04% N; found: 64.58% C, 4.72% H, 25.00% N. UV spectrum,  $\lambda_{\max}$ , nm, (log  $\epsilon$ ): 347 (3.43).  $^1\text{H}$  NMR spectrum: 6.91 (1 H, d,  $\text{C}_{(6)}\text{—H}$ ), 7.04 (1 H, d,  $\text{C}_{(9)}\text{—H}$ ), 7.28—7.80 (5 H, m,  $\text{H}_{\text{arom}}$ ), 2.31 (1 H, d,  $\text{C}_{(4)}\text{—CH}_3$ ),  $J_{6,9} = 0.8$  Hz).

1-Hydrazino-4-methyl-7-(4-tolyl)furo[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine (IVd). Yield 43%, m.p. 318°C (dioxane). For  $\text{C}_{16}\text{H}_{15}\text{N}_5\text{O}$  (293.3) calculated: 65.51% C, 5.15% H, 23.88% N; found: 65.51% C, 5.15% H, 23.80% N. UV spectrum,  $\lambda_{\max}$ , nm, (log  $\epsilon$ ): 352 (3.43).  $^1\text{H}$  NMR spectrum: 6.89 (1 H, d,  $\text{C}_{(6)}\text{—H}$ ), 6.95 (1 H, d,  $\text{C}_{(9)}\text{—H}$ ), 7.21, 7.65 (4 H, d,  $\text{H}_{\text{arom}}$ ), 2.29 (1 H, s,  $\text{C}_{(4)}\text{—CH}_3$ ), 2.20 (3 H, s,  $\text{C}_{\text{arom}}\text{—CH}_3$ ),  $J_{6,9} = 0.8$  Hz.

#### 9-Phenylfuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazolo[3,4-f]-1,2,4-triazine (Va)

The mixture of IVa (2.65 g, 10 mmol) and triethyl orthoformate (4 g, 28 mmol) in dimethylformamide (20 ml) was refluxed for 4 h, cooled and the separated crystals filtered off. Yield 2.14 g (78%), m.p. 296°C (dimethylformamide). For  $\text{C}_{15}\text{H}_9\text{N}_5\text{O}$  (275.3) calculated: 65.43% C, 3.29% H, 25.44% N; found: 65.32% C, 3.21% H, 25.36% N. UV spectrum,  $\lambda_{\max}$ , nm, (log  $\epsilon$ ): 344 (3.66), 237 (3.37).  $^1\text{H}$  NMR spectrum (trifluoroacetic acid): 7.30 (1 H, d,  $\text{C}_{(8)}\text{—H}$ ), 7.78 (1 H, dd,  $\text{C}_{(11)}\text{—H}$ ), 9.08 (1 H, d,  $\text{C}_{(3)}\text{—H}$ ), 9.11 (1 H, s,  $\text{C}_{(6)}\text{—H}$ ), 7.37—7.87 (5 H, m,  $\text{H}_{\text{arom}}$ ).

Following substances were synthesized in the same way:

9-Phenyl-3-methylfuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazolo[3,4-f]-1,2,4-triazine (Vb). Yield 76%, m.p. 309°C (dimethylformamide). For  $\text{C}_{16}\text{H}_{11}\text{N}_5\text{O}$  (289.3) calculated: 66.42% C, 3.83% H, 24.21% N; found: 66.32% C, 3.78% H, 24.02% N. UV spectrum,  $\lambda_{\max}$ , nm, (log  $\epsilon$ ): 347 (3.75), 237 (3.39).  $^1\text{H}$  NMR spectrum (trifluoroacetic acid): 7.21 (1 H, d,  $\text{C}_{(8)}\text{—H}$ ), 7.79 (1 H, d,  $\text{C}_{(11)}\text{—H}$ ), 9.08 (1 H, s,  $\text{C}_{(6)}\text{—H}$ ), 7.37—7.87 (5 H, m,  $\text{C}_{\text{arom}}\text{—H}$ ), 3.1 (3 H, s,  $\text{C}_{(3)}\text{—CH}_3$ ).

9-Phenyl-3,6-dimethylfuro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazolo[3,4-f]-1,2,4-triazine (Vc). Yield 79%, m.p. 32 °C (dimethylformamide). For  $C_{17}H_{13}N_5O$  (303.3) calculated: 67.32% C, 4.32% H, 23.09% N; found: 67.24% C, 4.36% H, 22.89% N. UV spectrum,  $\lambda_{max}$ , nm, (log  $\epsilon$ ): 344 (3.74), 237 (3.39).  $^1H$  NMR spectrum (difluoroacetic acid): 7.15 (1 H, d,  $C_{(8)}$ -H), 7.71 (1 H, d,  $C_{(11)}$ -H), 7.37-7.87 (5 H, m,  $C_{arom}$ -H), 2.94 (3 H, s,  $C_{(6)}$ -CH<sub>3</sub>), 3.16 (3 H, s,  $C_{(3)}$ -H).

9-(4-Tolyl)furo[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazolo[3,4-f]-1,2,4-triazine (Vd). Yield 78%, m.p. 306°C (dimethylformamide). For  $C_{16}H_{11}N_5O$  (289.3) calculated: 66.42% C, 3.83% H, 24.21% N; found: 66.32% C, 3.76% H, 24.17% N. UV spectrum,  $\lambda_{max}$ , nm, (log  $\epsilon$ ): 342 (3.36), 328 (3.94).  $^1H$  NMR spectrum (trifluoroacetic acid): 7.17 (1 H, d,  $C_{(8)}$ -H), 7.72 (1 H, dd,  $C_{(11)}$ -H), 9.02 (1 H, d,  $C_{(3)}$ -H), 9.03 (1 H, s,  $C_{(6)}$ -H), 7.22, 7.65 (4 H, d,  $H_{arom}$ ), 2.37 (3 H, s,  $C_{arom}$ -CH<sub>3</sub>).

3-Methyl-9-(4-tolyl)furo[2',3':4,5]pyrrolo[1,2-d]-1,2,5-triazolo[3,4-f]-1,2,4-triazine (Ve). Yield 76%, m.p. 32 °C (dimethylformamide). For  $C_{17}H_{13}N_5O$  (303.3) calculated: 67.32% C, 4.32% H, 23.09% N; found: 67.24% C, 4.16% H, 23.29% N. UV spectrum,  $\lambda_{max}$ , nm, (log  $\epsilon$ ): 347 (3.34), 238 (2.96).  $^1H$  NMR (trifluoroacetic acid): 7.12 (1 H, d,  $C_{(8)}$ -H), 7.79 (1 H, d,  $C_{(11)}$ -H), 9.04 (1 H, s,  $C_{(6)}$ -H), 7.22, 7.65 (4 H, d,  $H_{arom}$ ), 3.04 (3 H, s,  $C_{(3)}$ -CH<sub>3</sub>), 2.37 (3 H, s,  $C_{arom}$ -CH<sub>3</sub>).

#### N-Methoxycarbonyl-2-phenyl-4H-furo[3,2-b]pyrrole-5-carbohydrazide (VIa)

Methyl chloroformate (30 ml) and *Ia* (2.41 g, 10 mmol) were stirred and refluxed for 4 h, cooled, the precipitate filtered off, washed with ether, 5% sodium carbonate and water. Yield 2.48 g (83%), m.p. 258°C (dioxane). For  $C_{15}H_{13}N_3O_4$  (299.3) calculated: 60.19% C, 4.38% H, 14.04% N; found: 60.09% C, 4.20% H, 13.98% N. IR spectrum,  $cm^{-1}$ : 1 602, 1 700 (C=O). UV spectrum,  $\lambda_{max}$ , nm, (log  $\epsilon$ ): 339 (3.69), 234 (2.81).  $^1H$  NMR spectrum: 6.98 (1 H, d,  $C_{(3)}$ -H), 7.14 (1 H, dd,  $C_{(6)}$ -H), 7.36-7.85 (5 H, m,  $H_{arom}$ ), 9.15 (1 H, bs, N-H), 9.98 (1 H, bs, N-H), 11.5 (1 H, bs,  $N_{(4)}$ -H),  $J_{3,6} = 0.8$  Hz).

This procedure was employed for preparation of following substances:

N-Methoxycarbonyl-2-(4-tolyl)-4H-furo[3,2-b]pyrrole-5-carbohydrazide (VI). Yield 84%, m.p. 267°C (dioxane). For  $C_{16}H_{15}N_3O_4$  (313.3) calculated: 61.33% C, 4.83% H, 13.41% N; found: 61.30% C, 4.80% H, 13.57% N. IR spectrum,  $cm^{-1}$ : 1 637, 1 723 (C=O). UV spectrum,  $\lambda_{max}$ , nm, (log  $\epsilon$ ): 313 (3.07), 4.00 (3.05).  $^1H$  NMR spectrum: 6.93 (1 H, d,  $C_{(3)}$ -H), 7.04 (1 H, dd,  $C_{(6)}$ -H), 7.24, 7.69 (4 H, d,  $H_{arom}$ ), 9.15 (1 H, bs, N-H), 9.95 (1 H, bs, N-H), 11.46 (1 H, bs,  $N_{(4)}$ -H), 2.26 (3 H, s,  $C_{arom}$ -H,  $J_{3,6} = 0.8$  Hz).

#### 7-Phenyl-1,4-dioxo-1,2,3,4-tetrahydro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine (VIIa)

Hydrazide *VIa* (1 g, 4 mmol) added to a solution of potassium hydroxide (1.5 g) in ethanol (150 ml) was refluxed for 2.5 h, cooled and the precipitated salt dissolved in ethanol-water 1 : 1, filtered and precipitated with hydrochloric acid to a slightly acidic reaction. The precipitate was filtered off and dried. Yield 0.79 g (74%), m.p. 334°C (dioxane). For  $C_{14}H_9N_3O_3$  (267.2) calculated: 62.92% C, 3.39% H, 15.72% N; found: 62.72% C, 3.46% H, 15.64% N. IR spectrum,  $cm^{-1}$ : 1 686, 1 642 (C=O). UV spectrum,  $\lambda_{max}$ , nm, (log  $\epsilon$ ): 342 (3.58), 270 (2.88).  $^1H$  NMR spectrum: 6.69 (1 H, d,  $C_{(6)}$ -H), 7.60 (1 H, d,  $C_{(9)}$ -H), 7.38-7.94 (5 H, m,  $H_{arom}$ ).

Analogous procedures were employed for the synthesis of following compounds:

7-(4-Tolyl)-1,4-dioxo-1,2,3,4-tetrahydro[2',3':4,5]pyrrolo[1,2-d]-1,2,4-triazine (VIIb). Yield 76%, m.p. 349°C (dioxane). For  $C_{15}H_{11}N_3O_3$  (281.3) calculated: 64.04% C, 3.94% H, 14.94% N; found: 63.92% C, 3.98% H, 14.85% N. IR spectrum,  $cm^{-1}$ : 1 700, 1 643 (C=O). UV spectrum,

$\lambda_{\max}$ , nm (log  $\epsilon$ ): 342 (3.50), 270 (2.72).  $^1\text{H}$  NMR spectrum: 6.88 (1 H, d,  $\text{C}_{(6)}\text{-H}$ ), 7.44 (1 H, d,  $\text{C}_{(9)}\text{-H}$ ), 7.24, 7.76 (4 H, d,  $\text{H}_{\text{arom}}$ ), 2.28 (3 H, s,  $\text{C}_{\text{arom}}\text{-H}$ ),  $J_{6,9} = 0.8$  Hz.

### Spectral Measurements

The IR spectra of KBr discs were measured with a 71 IR spectrophotometer (Zeiss, Jena), the electronic absorption spectra of methanolic solutions with a Specord UV VIS (Zeiss, Jena) apparatus at  $1 \cdot 10^{-5}$ – $5 \cdot 10^{-5}$  mol  $\text{l}^{-1}$  concentration at room temperature. The  $^1\text{H}$  NMR spectra of hexadeuteriochloroform solutions (unless stated otherwise) were taken with a Tesla BS 487 C instrument operating at 80 MHz. Hexamethyldisiloxane and tetramethylsilane were the internal references when using deuteriochloroform and trifluoroacetic acid, respectively.

The mass spectra of some substances were run with an AEI MS 902 S spectrometer at an ionizing electron energy 70 eV, trap current 100  $\mu\text{A}$ ; the ionization locus temperature ranged between 80 and 210°C. The most prominent peaks and their relative intensities in parentheses for compound *IVd*: 293 ( $\text{M}^+$ , 100), 278 (37.2), 249 (23), 208 (51), 146 (7), 81 (7), 77 (32); *Va*: 275 ( $\text{M}^+$ , 100), 220 (9), 192 (6), 137 (10), 102 (7), 77 (8); *Vb*: 289 ( $\text{M}^+$ , 100), 219 (9), 193 (6.4), 164 (6.4); 144 (8), 102 (6), 77 (13); *Vc*: 303 ( $\text{M}^+$ , 100), 234 (13), 205 (6), 193 (8), 164 (6), 151 (9.8), 77 (10), *V*: 289 ( $\text{M}^+$ , 100), 233 (13), 144 (9), 105 (7), 77 (5).

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