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Condensed O-, N-Heterocycles by the Transformation of Azidoacrylates

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Summary. A number of furo[3,2-c]pyridines (**4a–4d**) and benzo[b]derivative (**4e**), as well as pyrrolo[2′,3′-4,5]furo[3,2-c]pyridine (**8**) were prepared by reaction of the corresponding iminophosphoranes, available from ethyl azidoheteroacrylates and triphenylphosphine, with phenyl isocyanate. The appropriate azidoheteroacrylates were used for the preparation of some substituted furo[3,2-b:4,5-b]dipyrroles (**6**). The reactions of the prepared compounds are described.

Keywords. Benzo[b]furo[3,2-c]pyridine; Furo[3,2-b:4,5-b′]dipyrroles; 4-(2-Nitrobenzyl)furo[3,2-b]pyrroles.

Kondensierte O-, N-Heterocyclen durch Umwandlung von Azidoacrylaten

Zusammenfassung. Eine Anzahl von Furo[3,2-c]pyridinen (**4a–4d**), ein Benzo[b]derivat (**4e**) und Pyrrolo[2′,3′:4,5]furo[3,2-c]pyridin (**8**) wurden durch die Reaktion von Phenylisocyanaten mit den entsprechenden Iminophosphoranen dargestellt, die aus Ethyl-azidoheteroacrylaten und Triphenylphosphin leicht zugänglich sind. Die entsprechenden Azidoacrylate wurden zur Synthese einiger Furo[3,2-b:4,5-b′]dipyrrole (**6**) verwendet. Die Reaktionen einiger dieser Verbindungen werden beschrieben.

Introduction

The first paper [1] dealing with the synthesis of a furo[3,2-b]pyrrole derivative published in this journal, stimulated our studies in this area. By modification of the method described in [1], a series of 2-substituted furo-[3,2-b]pyrrole derivatives from 5-substituted-2-furancarbaldehydes were prepared [2–6]. Several reaction centers of ethyl 2-substituted furo-[3,2-b]pyrrole-5-carboxylates were studied and utilized in the synthesis of new heterocyclic systems [7–10]. The papers [11–12] present the formylation, nitration, Mannich reaction and copulation of variously substituted furo[3,2-b]pyrroles or their benzo[b]derivatives. The studies [13–15] of addition and cycloaddition reactions of furo[3,2-b]pyrroles and their condensed derivatives showed that their reaction course is influenced by the substituents attached to this system.

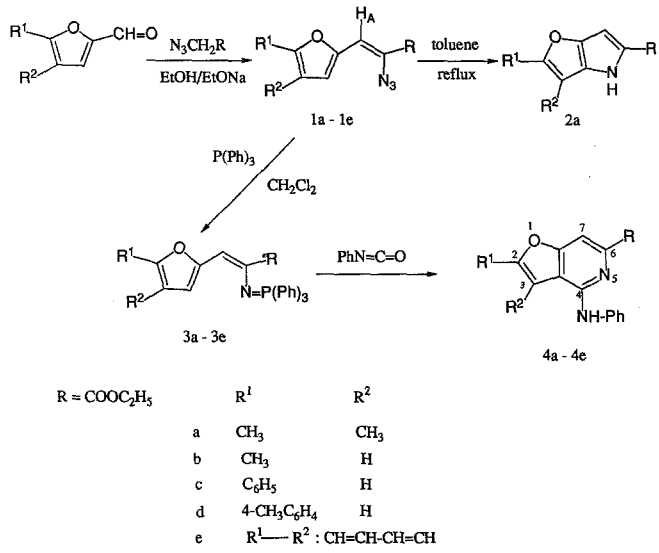
Several methods have been described [16] for the synthesis of the furo[3,2-

c]pyridine system, starting either from pyridines or furans [16–20]. Electrophilic [21], nucleophilic [22] reactions and biological properties [23] of furo[3,2-c]pyridines were studied.

Results and Discussion

In continuation of our previous efforts towards the preparation of condensed O-, N-heterocycles we here report efficient syntheses of some representatives of the title ring systems, employing 4,5-dimethyl-, 5-methyl-, 5-phenyl-, 5-(4-methylphenyl)-2-furancarbaldehyde and benzo[b]furan-2-carbaldehyde.

Reaction of 4,5-dimethyl-2-furancarbaldehyde with ethyl azidoacrylate in the presence of a sodium ethoxide was found (Scheme 1) to proceed smoothly to give **1a**, the thermolysis of which was carried out in boiling toluene leading to ethyl 2,3-dimethylfuro[3,2-b]pyrrole-5-carboxylate (**2a**). This reaction was relatively rapid and afforded the product in very good yield. Further the compound **1a** reacted with triphenylphospine in dry dichloromethane to give iminophosphorane **3a** in very good yield. Then iminophosphoranes **3b–3e** were prepared analogically starting from the corresponding azidoheteroacrylates [2, 5, 24].



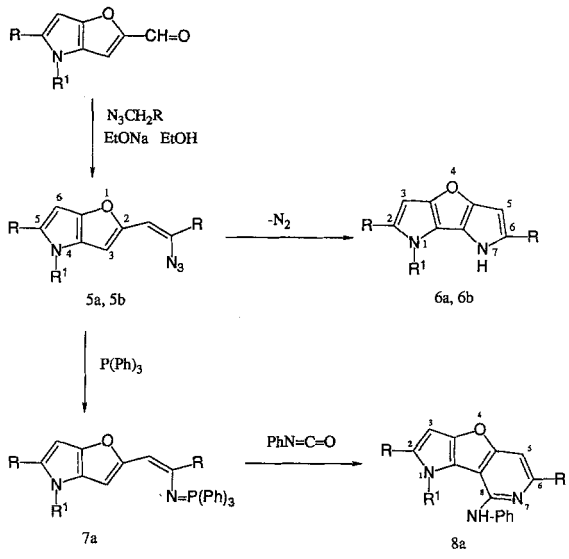
R = $COOC_2H_5$	R^1	R^2
a	CH_3	CH_3
b	CH_3	H
c	C_6H_5	H
d	4-$CH_3C_6H_4$	H
e	R^1—R^2 : CH=CH-CH=CH	

Scheme 1

Compounds **3a–3e** reacted with phenyl isocyanate in dry toluene under reflux to give triphenylphosphine oxide and the corresponding substituted furo[3,2-b]pyridines (**4a–4d**) and benzo[b]furo[3,2-b]pyridine (**4e**) via appropriate carbodiimides which were not isolated.

Starting from aldehydes furo[3,2-b]pyrrole type (Scheme 2) by an analogous way as **1a**, the compounds **5a**, **5b** were made. The thermolysis of **5a** and **5b** in boiling toluene gave **6a** and **6b**. By treatment of **5a** with triphenylphosphine in dry dichloromethane iminophosphorane **7a** arose, which by the reaction with phenyl isocyanate gave substituted pyrrolo[2′,3′:4,5]furo[3,2-c]pyridines.

The hydrolysis of **1a** furnished the corresponding acid **9a** (Scheme 3).

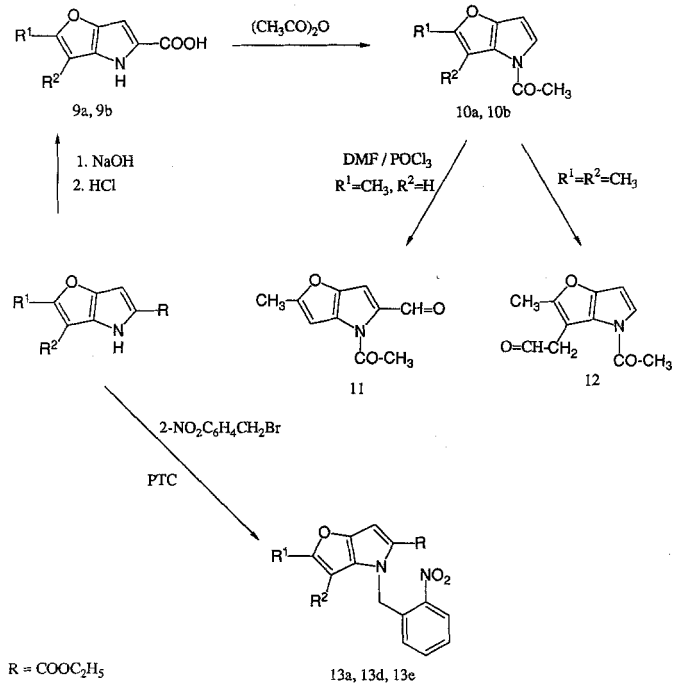


R = $COOC_2H_5$

For compounds a R^1 = CH_3

b R^1 = CH_2Ph

Scheme 2



R = $COOC_2H_5$

For compounds a R^1=R^2= CH_3

b R^1= CH_3 R^2= H

c R^1= $CH_3C_6H_4$ R^2= H

d R^1---R^2 = CH=CH- CH=CH

Scheme 3

One of the most interesting results in this area is acetylative decarboxylation of the acids **9a**, **9b** giving 4-acetylated products **10a**, **10b**. We suppose that during heating in boiling acetic anhydride the acetylation takes place in the first step. The presence of an acetyl group at the nitrogen atom of substituted furo[3,2-b]pyrrole-5-carboxylic acids (**9a**, **9b**) increases their acidity and consequently the temperature of the reaction medium becomes sufficient for their decarboxylation.

The mentioned compounds **10a**, **10b** were formylated under condition of Vilsmeier reaction. The compound **10b** yielded the 5-formylated product **11**. We expected a similar product in the case of **10a**, but the ^{1}H-NMR spectrum indicated that the reaction at the methyl group attached at C-3 of the furo[3,2-b]pyrrole system lead to disappearance of this resonance giving a doublet for 2 H at 2.81 ppm instead (compound **12**, methylene group).

The phase transfer catalysis was found to be successful for the N-2-nitrobenzylation of the furo[3,2-b]pyrrole system under milder conditions then used in our previous works [3, 5]. Compounds of type **13** were used for the synthesis a new condensed heterocyclic system – furo[2′,3′:4,5]pyrrolo[2,1-c][1,4]benzodiazepine [25], which is close to indolo[2,1-c][1,4]benzodiazepines belonging to a class antiallergic agents [26].

Experimental Part

Melting points were determined on a Kofler hot plate apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a Tesla BS 487 C (80 MHz) spectrophotometer (*TMS* as internal standard, $CDCl_3$ or $(CD_3)_2CO$, δ values in ppm, J in Hz). UV spectra were measured on a M-40 (Carl Zeiss Jena) spectrophotometer in ethanol ($\lambda_{max}/\log\varepsilon$; λ_{max} in nm, ε in $m^2 mol^{-1}$). The IR spectra were recorded on a FTIR PU 9802/25 (Philips) spectrophotometer using KBr technique (0.5 mg/300 mg KBr) (ν_{max} in cm^{-1}).

The following starting compounds were prepared: 5-phenyl-2-furancarbaldehyde and 5-(4-methylphenyl)-2-furancarbaldehyde [27]; benzo[b]furan-2-carbaldehyde [24]; 4,5-dimethyl-2-furancarbaldehyde [28] ethyl 2-azido-3-(5-methyl-2-furyl)acrylate and ethyl 2-methylfuro[3,2-b]pyrrole-5-carboxylate according to [5]; ethyl 2-azido-3-(5-phenyl-2-furyl)acrylate, 2-phenylfuro[3,2-b]pyrrole-5-carboxylate, ethyl 2-azido-3-[5-(4-methylphenyl)-2-furyl]acrylate and ethyl 2-(4-methylphenyl)-furo[3,2-b]pyrrole-5-carboxylate according to [2]; ethyl 2-formyl-4-methyl-furo[3,2-b]pyrrole-5-carboxylate [11]; ethyl 4-benzylfuro[3,2-b]pyrrole-5-carboxylate [25].

Ethyl 2-Azido-3-(4,5-dimethyl-2-furyl)acrylate (**1a**)

A solution of 4,5-dimethyl-2-furancarbaldehyde (2.84 g, 0.02 mol) and ethyl azidoacetate (6.3 g, 0.05 mol) was added at 0°C during 30 min to sodium metal (1.84 g, 0.08 gat) in ethanol (60 ml). Stirring was continued for additional 60 min at a temperature not exceeding 5°C, the reaction mixture was then cooled to 0°C, a solution of ammonium chloride (2.1 g, 0.04 mol) in water (10 ml) was added and poured in ice water. The separated precipitate was filtered off and crystallized. Yield 3.43 g (73%); m.p. 51 – 52°C (ethanol). For $C_{11}H_{13}N_3O_3$ (235.2) calc.: C 56.16, H 5.57, N 17.86; found: C 55.98, H 5.60, N 17.90. ^{1}H-NMR ($CDCl_3$): 1.36 (t, 3 H, CH_3), 1.97 (s, 3 H, C-5-CH_3), 2.24 (s, 3 H, C-4-CH_3), 4.31 (q, 2 H, CH_2), 6.78 (s, 1 H, H-A), 6.92 (s, 1 H, H-3).

Ethyl 2,3-Dimethylfuro[3,2-b]pyrrole-5-carboxylate (**2a**)

Ethyl 2-azido-3-(4,5-dimethyl-2-furyl)acrylate (**1a**) (1 g, 0.04 mol) was dissolved in toluene (100 ml). The mixture was refluxed under stirring for 1 h, the solvent was evaporated in vacuo and the product

was crystallized. Yield 0.77 g (88%); m.p. 207–208°C (ethanol). For $C_{11}H_{13}NO_3$ (207.2) calc.: C 63.75, H 6.32, N 6.76; found: C 63.72, H 6.28, N 6.70. ^{1}H-NMR ($CDCl_3$): 1.36 (t, 3H, CH_2), 2.08 (d, 1H, C-3-CH_3), 2.33 (s, 1H, C-2-CH_3), 4.33 (q, 2H, CH_2), 6.69 (d, 1H, H-6), 8.83 (bs, 1H, H-4); J(3,4) = 0.88, J(4,5) = 1.76.

Ethyl 2-Triphenylphosphoimino-3-(4,5-dimethyl-2-furyl)acrylate (**3a**)

A solution of triphenylphosphine (1.31 g, 0.005 mol) in dry dichloromethane (20 ml) was added dropwise under nitrogen to a stirred solution of **1a** (1.17 g, 0.005 mol) in the same solvent (10 ml) at 0°C. The reaction mixture was allowed to warm to room temperature and stirring was continued for 20 h. The solvent was removed under reduced pressure and the residual solid was recrystallized to give **3a**. Yield 1.92 g (82%); m.p. 115–117°C (toluene/*n*-hexane 1 : 1). For $C_{28}H_{28}NO_3P$ (469.5) calc.: C 74.19, H 6.01, N 2.98; found: C 74.26, H 6.06, N 2.92. ^{1}H-NMR [$(CD_3)_2CO$]: 0.9 (t, 1H, CH_3), 1.39 (s, 1H, C-4-CH_3), 3.82 (q, 2H, CH_2), 6.61 (d, 1H, H-A), 6.95 (s, 1H, H-3), 7.44–7.92 (m, 15H, H-arom); J(A,P) = 7.65.

Using the same method the compounds **3b–3e** were prepared:

Ethyl 2-Triphenylphosphoimino-3-(5-methyl-2-furyl)acrylate (**3b**)

Yield 95%; m.p. 136–139°C (toluene/*n*-hexane 1 : 1). For $C_{28}H_{26}NO_3P$ (455.3) calc.: C 73.83, H 5.76, N 3.07, found: C 73.80, H 5.68, N 3.12. ^{1}H-NMR [$(CD_3)_2CO$]: 0.98 (t, 3H, CH_3), 2.29 (s, 3H, C-5-CH_3), 3.82 (q, 2H, CH_2), 6.04 (d, 1H, H-4), 6.63 (d, 1H, H-A), 7.02 (d, 1H, H-3); J(3,4) = 3.84, J(A,P) = 7.65.

Ethyl 2-Triphenylphosphoimino-3-(5-phenyl-2-furyl)acrylate (**3c**)

Yield 87%; m.p. 74–75°C (toluene/*n*-hexane 1 : 1). For $C_{33}H_{28}NO_3P$ (517.5) calc.: C 76.59, H 5.45, N 2.71; found: C 76.40, H 5.38, N 2.68. ^{1}H-NMR ($CDCl_3$): 1.10 (t, 3H, CH_3), 3.87 (q, 2H, CH_2), 5.29 (s, 1H, H-4), 6.69 (d, 1H, H-A), 7.26 (s, 1H, H-3), 7.36–7.94 (m, 20H, H-arom); J(A,P) = 6.8.

Ethyl 2-Triphenylphosphoimino-3-[5-(4-methylphenyl)-2-furyl]acrylate (**3d**)

Yield 84%; m.p. 175–176°C (toluene/hexane 1 : 1). For $C_{34}H_{30}NO_3P$ (531.6) calc.: C 76.82, H 5.69, N 2.63; found: C 76.76, H 5.64, N 2.68. ^{1}H-NMR ($CDCl_3$): 1.01 (t, 3H, CH_3), 2.34 (s, 1H, CH_3), 3.87 (q, 2H, CH_2), 6.69 (d, 1H, H-4), 7.35–7.86 (m, 19H, H-arom); J(3,4) = 3.82; J(A,P) = 6.76.

Ethyl 2-Triphenylphosphoimino-3-(2-benzo[b]furyl)acrylate (**3e**)

Yield 88%; m.p. 135–137°C (toluene/*n*-hexane 1 : 1). For $C_{31}H_{26}NO_3P$ (491.3) calc.: C 75.75, H 5.33, N 2.85; found: C 75.79, H 5.26, N 2.80. ^{1}H-NMR ($CDCl_3$): 1.04 (t, 3H, CH_3), 3.89 (q, 2H, CH_2), 6.82 (q, 2H, CH_2), 6.82 (d, 1H, H-A), 7.26 (s, 1H, H-3), 7.44–7.80 (m, 19H, H-arom); J(A,P) = 6.61.

Ethyl 2,3-Dimethyl-4-phenylaminofuro[3,2-c]pyridine-6-carboxylate (**4a**)

A solution of the phenyl isocyanate (0.60 g, 0.005 mol) in dry toluene (50 ml) was added dropwise under nitrogen to stirred solution of **3a** (2.34 g, 0.005 mol). The reaction mixture was refluxed for 12 h. The solvent was removed under reduced pressure and the solid residue was crystallized. Yield 0.63 g (41%); m.p. 150–153°C (ethanol). For $C_{18}H_{18}N_2O_3$ (310.3) calc.: C 69.67, H 5.85, N 9.03; found: C 69.48, H 5.80, N 9.09. ^{1}H-NMR [$(CD_3)_2CO$]: 1.41 (t, 3H, CH_3), 2.43 (s, 3H, C-3-CH_3), 2.51 (s, 3H, C-2-CH_3), 4.37 (q, 2H, CH_2), 6.96–8.08 (m, 6H, H-arom), 7.67 (s, 1H, H-7).

Using the same method the compounds **4b–4e** were prepared:

Ethyl 2-Methyl-4-phenylaminofuro[3,2-c]pyridine-6-carboxylate (**4b**)

Yield 45%; m. p. 136–138°C (ethanol). For $C_{17}H_{16}N_2O_3$ (296.3) calc.: C 68.90, H 5.44, N 9.45; found: C 68.78, H 5.48, N 9.38. ^{1}H-NMR [$(CD_3)_2CO$]: 1.46 (t, 3H, CH_3), 2.25 (d, 3H, C-2-CH_3), 4.55 (q, 2H, CH_2), 7.04–7.95 (m, 6H, H-arom), 7.53 (dd, 1H, H-3), 7.58 (d, 1H, H-7); $J(2, 3) = 0.88$, $J(3, 7) = 0.76$.

Ethyl 2-Phenyl-4-phenylaminofuro[3,2-c]pyridine-6-carboxylate (**4c**)

Yield 42%; m. p. 196–198°C (ethanol). For $C_{22}H_{18}N_2O_3$ (358.4) calc.: C 73.73, H 5.06, N 7.81; found: C 73.69, H 4.98, N 7.78. ^{1}H-NMR [$(CD_3)_2CO$]: 1.44 (t, 3H, CH_3), 4.49 (q, 2H, CH_2), 7.24–7.53 (m, 10H, H-arom), 7.59 (d, 1H, H-3), 7.82 (d, 1H, H-3), 7.82 (d, 1H, H-7), 8.62 (s, 1H, NH); $J(3,7) = 0.76$.

Ethyl 2-(4-Methylphenyl)-4-phenylaminofuro[3,2-c]pyridine-6-carboxylate (**4d**)

Yield 43%; m. p. 162–167°C (ethanol). For $C_{23}H_{20}N_2O_3$ (372.4) calc.: C 74.18, H 5.41, N 7.52; found: C 74.53, H 5.15, N 7.93. ^{1}H-NMR ($CDCl_3$): 1.45 (t, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.44 (q, 2H, CH_2), 7.36 (d, 1H, H-3), 7.41–7.65 (m, 9H, H-arom), 7.73 (s, 1H, NH), 7.82 (d, 1H, H-7); $J(3,7) = 0.76$.

Ethyl 1-Phenylaminobenzo[b]furo[3,2-c]pyridine-3-carboxylate (**4e**)

Yield 49%; m. p. 154–156°C (ethanol). For $C_{20}H_{16}N_2O_3$ (332.4) calc.: C 72.27, H 4.85, N 8.42; found: C 72.34, H 5.91, N 8.54. ^{1}H-NMR ($CDCl_3$): 1.41 (t, 3H, CH_3), 4.39 (q, 2H, CH_3), 7.07–7.65 (m, 9H, H-arom), 7.64 (s, 1H, NH), 7.83 (s, 1H, H-7).

Ethyl 2-Azido-3-[(5-ethoxycarbonyl-4-methyl)furo[3,2-b]-2-pyrryl]acrylate (**5a**) *and Ethyl 2-Azido-3-[(4-benzyl-5-ethoxycarbonyl)furo[3,2-b]-2-pyrryl]acrylate* (**5b**)

5a and **5b** were prepared according to the procedure used for **1a**.

5a: Yield 85%; m. p. 118–119°C (ethanol). For $C_{15}H_{16}N_4O_5$ (332.3) calc.: C 54.22, H 4.85, N 16.86; found: C 54.20, H 5.13, N 16.71. ^{1}H-NMR [$(CD_3)_2CO$]: 1.29 (t, 3H, CH_3), 1.34 (t, 3H, CH_3), 4.12 (s, 1H, N-CH_3), 4.20 and 4.21 (q, 2H, 2H, CH_2), 6.76 (s, 1H, H-A), 6.81 and 6.84 (s, 1H, 1H, H-3, H-6).

5b: Yield 84%; m. p. 97°C (ethanol). For $C_{21}H_{20}N_4O_5$ (408.4) calc.: C 61.76, H 4.94, N 13.72; found: C 61.31, H 4.87, N 13.48. ^{1}H-NMR (*DMSO-d_6*): 1.32 (t, 3H, CH_3), 1.36 (t, 3H, CH_3), 4.28 and 4.33 (q, 2H, 2H, CH_2), 5.65 (s, 2H, CH_2*Ph*), 6.78 (s, 1H, H-A), 6.85 and 6.89 (s, 1H, 1H, H-3, H-6), 7.25–7.27 (m, 5H, H-arom).

Diethyl 1-Methyl-7H-furo[3,2-b:4,5-b']dipyrrole-2,6-dicarboxylate (**6a**) *and Diethyl 1-Benzyl-7H-furo[3,2-b:4,5-b']dipyrrole-2,6-dicarboxylate* (**6b**)

6a and **6b** were prepared according to the procedure used for **2a**.

6a: Yield 43%; m. p. 227–228°C (ethanol). For $C_{15}H_{16}N_2O_5$ (304.3) calc.: C 59.20, H 5.30, N 9.20; found: C 58.90, H 5.06, N 9.39. ^{1}H-NMR (*DMSO-d_6*): 1.30 (t, 3H, CH_3), 1.36 (t, 3H, CH_3), 4.12 (s, 3H, N-CH_3), 4.23 and 4.28 (q, 2H, 2H, CH_2), 6.81 and 6.84 (s, 1H, 1H, H-3, H-5).

6b: Yield 45%; m. p. 169–171°C (ethanol). For $C_{21}H_{20}N_2O_5$ (380.4) calc.: C 66.30, H 5.30, N 7.36; found: C 66.01, H 5.39, N 7.80. ^{1}H-NMR [$(CD_3)_2CO$]: 1.28 (t, 3H, CH_3), 1.31 (t, 3H, CH_3), 4.23 and 4.28 (q, 2H, 2H, CH_2), 5.90 (s, 2H, CH_2Ph), 6.87 (d, 1H, H-5), 7.25 (s, 1H, H-3), 7.27-7.31 (m, 5H, H-arom), 10.82 (bs, 1H, NH).

Ethyl 2-Triphenylphosphoimino-3-[(4-methyl-5-ethoxycarbonyl)furo[3,2-b]-2-pyrryl]acrylate (**7a**)

Prepared according to the procedure used for **3a**. Yield 51%; m.p. 124–127°C (toluene/*n*-hexane 1:1). For $C_{33}H_{31}N_2O_5P$ (566.6) calc.: C 69.95, H 5.51, N 4.94; found: C 69.98, H 5.47, N 4.95. ^{1}H-NMR [$(CD_3)_2CO$]: 1.30 (t, 3H, CH_3), 1.34 (t, 3H, CH_3), 4.15 (s, 1H, N-CH_3), 4.24 (q, 2H, 2H, CH_2), 6.61 (d, 1H, H-A), 6.84 and 6.87 (s, 1H, 1H, H-3, H-6), 7.47–7.90 (m, 15H, H-arom); J(A,P) = 7.32.

Diethyl 1-Methyl-8-phenylaminopyrrolo[2',3':4,5]furo[3,2-c]pyridine-2,6-dicarboxylate (**8a**)

Prepared according to the procedure used for **4a**. Yield 53%; m.p. 176–177°C (ethanol). For $C_{22}H_{21}N_3O_5$ (407.4) calc.: C 64.86, H 5.19, N 10.31; found: C 64.82, H 5.27, N 10.52. ^{1}H-NMR [$(CD_3)_2CO$]: 1.28 (t, 3H, CH_3), 1.37 (t, 3H, CH_3), 4.12 (s, 3H, N-CH_3), 4.17 (q, 2H, CH_2), 4.33 (q, 2H, CH_2), 6.75 (s, 1H, H-3), 6.81 (s, 1H, NH), 7.07–7.15 (m, 6H, H-arom). IR: 3463 (NH), 3144 (=CH)pyrrole, 3100 (=CH)pyridine, 3048 (=C-N)pyridine, 1597, 1593, 1576, 1549, 1526 (C=C)arom.

2,3-Dimethylfuro[3,2-b]pyrrole-5-carboxylic Acid (**9a**)

Compound **2a** (2.07 g, 0.01 mol) in ethanol (50 ml) and 5% sodium hydroxide (20 ml) was heated on a steam bath for 1 h and concentrated to half of its original volume. The precipitate was dissolved in dilute ethanol (50%), acidified with hydrochloric acid 1:1 and poured into ice. Yield 72%; m.p. 142–146°C (ethanol). For $C_9H_9NO_3$ (179.1) calc.: C 60.33, H 5.06, N 7.83; found: C 60.54, H 5.30, N 7.68. ^{1}H-NMR (*DMSO-d_6*): 2.03 (s, 3H, C-3-CH_3), 2.26 (s, 3H, C-2-CH_3), 6.38 (s, 1H, H-6), 10.99 (s, 1H, NH). IR: 1620 (C=O).

2,3-Dimethyl-4-acetylfuro[3,2-b]pyrrole (**10a**)

Compound **9a** (1.79 g, 0.01 mol) in acetanhydride (30 ml) was refluxed for 4 h, than acetanhydride was distilled of under reduced pressure. The crude product was crystallized. Yield 0.44g (40%); m.p. 41.5–42.5°C (*n*-hexane). For $C_{10}H_{11}NO_2$ (177.2) calc.: C 67.78, H 6.26, N 7.90; found: C 67.64, H 6.22, N 7.54. ^{1}H-NMR [$(CD_3)_2CO$]: 2.24 (s, 3H, C-3-CH_3), 2.28 (s, 3H, C-2-CH_3), 2.55 (s, 3H, $COCH_3$), 6.25 (d, 1H, H-6), 7.18 (d, 1H, H-5); J(5,6) = 3.5. IR: 1697 (C=O).

2-Methyl-4-acetylfuro[3,2-b]pyrrole (**10b**)

Prepared in analogy to **10a**. Yield 75%; m.p. 30–32°C (*n*-hexane). For $C_9H_9NO_2$ (163.1) calc.: C 66.24, H 5.56, N 8.58; found: C 66.14, H 5.48, N 8.48. ^{1}H-NMR [$(CD_3)_2CO$]: 2.35 (d, 3H, CH_3), 2.51 (s, 3H, $COCH_3$), 6.30 (dd, 1H, H-6), 6.40 (d, 1H, H-3), 7.03 (d, 1H, H-5); J(3,6) = 0.8, J(5,6) = 3.4. IR: 1720 (C=O).

2-Methyl-4-acetylfuro[3,2-b]pyrrole-5-carbaldehyde (**11**)

Dimethylformamide (3 g, 0.04 mol) and phosphorus oxychloride (3.4 g, 0.011 mol) were stirred at 0°C for 20 min. A solution of **10b** (1.63 g, 0.01 mol) in dimethylformamide (3 ml) was added to this mixture so as the temperature did not exceed 10°C. The stirring was continued at 5°C for 1 h, at 20°C for the additional 1 h; the content was poured into ice-cold water and neutralized with sodium hydrogen carbonate. The product was filtered off and crystallized. Yield 0.96 g (50%); m.p. 131–133°C (ethanol). For $C_{10}H_9NO_3$ (191.2) calc.: C 62.82, H 4.74, N 7.32; found: C 62.76, H 4.58, N 7.18. ^{1}H-NMR [$(CD_3)_2CO$]: 2.46 (s, 3H, CH_3), 2.72 (s, 3H, $COCH_3$), 6.31 (d, 1H, H-3), 7.1 (d, 1H, H-6), 10.28 (s, 1H, CHO); J(3,6) = 0.88. IR: 1732 ($COCH_3$), 1676, 1657 (CH=O).

2-Methyl-3-formylmethyl-4-acetylfuro[3,2-b]pyrrole (**12**)

Starting from **10a** under the same conditions as for **11**, compound **12** was obtained. Yield 31%; m. p. 84–87°C (ethanol). For $C_{11}H_{11}NO_3$ (205.2) calc.: C 64.38, H 5.40, N 6.82; found: C 64.24, H 5.28, N 6.90. ^{1}H-NMR [$(CD_3)_2CO$]: 2.31 (s, 1 H, C-2-CH_3), 2.54 (s, 3 H, $COCH_3$), 2.81 (d, 2 H, CH_2), 6.33 (d, 1 H, H-6), 7.24 (d, 1 H, H-5), 9.20 (t, 1 H, J = 1.32, CHO); J(5,6) = 3.57. IR: 1 725 ($COCH_3$), 1 688 (CH=O).

Ethyl 2,3-Dimethyl-4-(2-nitrobenzyl)furo[3.2-b]pyrrole-5-carboxylate (**13a**)

Compound **2a** (4.14 g, 0.02 mol) in toluene (200 ml) was poured into a 32% aqueous solution of sodium carbonate and while stirred 2-nitrobenzylbromide (4 g, 0.021 mol) and tetrabuthylammonium bromide (1.7 g, 0.005 mol) were added. The reaction mixture was kept stirred at 60°C for 50 h, than it was cooled and diluted with water. The organic layer was separated and the aqueous one extracted with ether. The combined organic solutions were washed with water and dried with anhydrous sodium sulfate. The work up gave **13a**. Yield 1.36 g (20%); m. p. 132–134°C (ethanol). For $C_{18}H_{18}N_2O_5$ (342.3) calc.: C 63.15, H 5.30, N 8.19; found: C 63.51, H 5.39, N 8.19. ^{1}H-NMR [$(CD_3)_2CO$]: 1.20 (t, 3 H, CH_3), 2.40 (s, 3 H, C-3-CH_3), 2.79 (s, 3 H, C-2-CH_3), 4.13 (q, 2 H, CH_2), 6.10 (s, 2 H, CH_2Ph), 6.83 (s, 1 H, H-6), 7.35–7.65 (m, 4 H, H-arom). IR: 1 335 $(NO_2)_s$, 1 572 $(NO_2)_{as}$, 1 580, 1 611 (C=C), 1 688 (C=O). UV: 310.6 (2.68).

By the same method compounds **13d** and **13e** were prepared:

Ethyl 2-(4-Methylphenyl)-4-(2-nitrobenzyl)furo[3,2-b]pyrrole-5-carboxylate (**13d**)

Yield 89%; m. p. 162–167°C (ethanol). For $C_{23}H_{20}N_2O_5$ (403.4) calc.: C 68.22, H 4.99, N 6.94; found: C 67.96, H 5.01, N 6.76. ^{1}H-NMR [$(CD_3)_2CO$]: 1.08 (t, 3 H, CH_3), 2.24 (s, 1 H, $CH_3C_6H_4$), 4.02 (q, 2 H, CH_2), 5.94 (s, 2 H, CH_2Ph), 6.84 (s, 1 H, H-6), 6.88 (s, 1 H, H-3), 7.06–7.58 (m, 8 H, H-arom). IR: 1 335 $(NO_2)_s$, 1 522 $(NO_2)_{as}$, 1 578, 1 607 (C=C), 1 689 (C=O). UV: 260.7 (2.53), 322.6 (2.83).

Ethyl 1-(2-Nitrobenzyl)-benzo[b]furo[3,2-b]pyrrole-2-carboxylate (**13e**)

Yield 81%; m. p. 197–200°C (ethanol). For $C_{20}H_{16}N_2O_5$ (364.4) calc.: C 65.93, H 4.43, N 7.69; found: C 65.82, H 4.30, N 7.60. ^{1}H-NMR (*DMSO-d_6*): 1.04 (t, 3 H, CH_3), 4.07 (q, 2 H, CH_2), 6.23 (s, 2 H, CH_2Ph), 7.05 (s, 1 H, H-6), 7.15–8.19 (m, 8 H, H-arom). IR: 1 331 $(NO_2)_s$, 1 526 $(NO_2)_{as}$, 1 576, 1 610 (C=C), 1686 (C=O). UV: 260.7 (2.53), 322.6 (2.83).

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