SYNTHESIS AND REACTIONS
OF SUBSTITUTED BENZOFURO[3,2-b]PYRROLE DERIVATIVES*

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This paper deals with the preparation of ethyl benzofuro[3,2-b]-pyrrole-2-carboxylate, its hydrolysis, N-alkylation, and reduction. Also the synthesis of new heterocyclic systems, benzofuro-[3,2-b]pyrrole and 2H-dihydrobenzofuro[2′,3′:4,5]pyrrolo[1,2-d]1,2,4-triazin-1-one, is described. The structure of 14 new substances was corroborated by IR, UV ^1H NMR, ^{13}C NMR and electron impact mass spectra.

Our preceding papers[1−4] concerned the investigation of condensation reaction of ethyl azidoacetate with aldehydes derived from furan, as well as cyclization of thus prepared substituted vinyl azides to 2-substituted ethyl furo[3,2-b]pyrrole-5-carboxylates and some of their reactions. This paper describes the reaction of 3-benzofurancarbaldehyde with ethyl azidoacetate leading to ethyl 2-azido-3-(2-benzofuryl)acrylate (*I*), the thermolysis of which afforded ethyl benzofuro[3,2-b]pyrrole-2-carboxylate (*II*). The corresponding hydrazide *III* was obtained by reacting *II* with hydrazine hydrate in excess; this compound having two reaction centres enables to carry out a cyclization reaction yielding the corresponding triazine (Scheme 1). Recently, several authors[5−11] have paid attention to the synthesis of heterocyclic compounds, having the 1,2,4-triazine ring embodied in their molecules and showing biological activity. An analogous type was now prepared by reaction of *III* with ethyl orthoformate, or orthoacetate; the synthesized 2H-dihydrobenzofuro[2′,3′:4,5]-pyrrolo[1,2-d]1,2,4-triazin-1-one (*IV*), or its $C_{(4)}$ methylated derivative *V* are being biologically tested.

Ethyl benzofuro[3,2-b]pyrrole-2-carboxylate was the starting material for preparation of a series of compounds *VI − XIV*.

Compound *I* gave *VI* with methyl iodide in the presence of triethylbenzylammonium bromide under conditions of phase-transfer catalysis[12,13]. The reaction proceeded in good yields within a short reaction time, this being a great advantage when compared with alkylation using N-alkali metal salts. Cyanoethylation of *I* was

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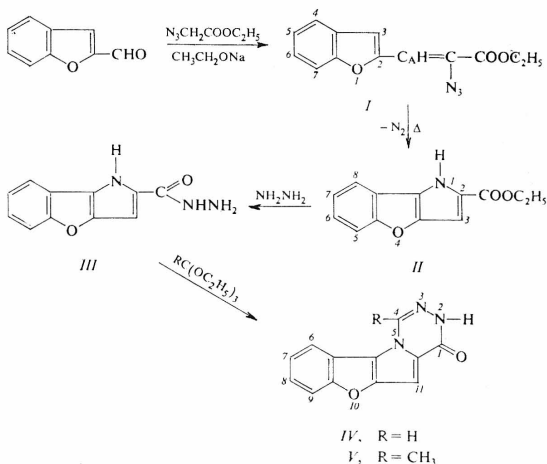
SCHEME 1
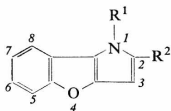
VI, $R^1 = CH_3$; $R^2 = COOC_2H_5$ XI, $R^1 = R^2 = H$
VII, $R^1 = CH_3$; $R^2 = CONHNH_2$ XII, $R^1 = CH_3$; $R^2 = H$
VIII, $R^1 = CH_2CH_2CN$; $R^2 = COOC_2H_5$ XIII, $R^1 = H$; $R^2 = CH_3$
IX, $R^1 = H$; $R^2 = COOH$ XIV, $R^1 = CH_3$; $R^2 = CH_2OH$
X, $R^1 = CH_3$; $R^2 = COOH$

carried out in a similar way using trimethylbenzylammonium hydride as catalyst with the difference that it did not proceed in two phases. Hydrolysis of esters II and VI furnished salts of the corresponding acids showing different stabilities. Sodium salts of 1-methyl derivative is more photostable than that derived from IX. Sodium salts of acids IX and X crystallized from 50% ethanol as trihydrates; these were employed for determination of pK_A constants of compounds IX and X. Acids IX and X were decarboxylated in quinoline in the presence of copper chromite barium promoted. Acid IX was found to be best decarboxylated within $120-122°C$ and its methylated analogue X at $150-155°C$. These differences were evidently

caused by a different acidity of these acids and were in agreement with their pK_A values.

The new heterocyclic system prepared by decarboxylation of *IX* was studied under conditions of an electrophilic substitution. Acetylation with acetic anhydride was investigated in dichloromethane at 50°C, and at its boiling point temperature, at 100°C without any solvent and at the boiling point of acetic anhydride. None the less, even after a 8 h-reaction only the starting material was isolated. Benzofuro[3,2-*b*]pyrrole evidently showed a decreasing tendency to undergo substitution reactions when compared with pyrrole[14]. Reduction of esters *II* and *VI* with lithium hydridoaluminate (under the same reaction conditions: boiling ether, 1·5 h) furnished two different products. Whereas reduction of *II* afforded 2-methylbenzofuro[3,2-*b*]-pyrrole (*XIII*, reduction of *VI* yielded the 2-hydroxymethyl analogue *XIV*. This result is associated with the electron-donating effect of the methyl group located in position 1 of compound *VI*.

All synthesized compounds exhibit characteristic $v(C=C)_{arom}$ vibrations at 1 525 to 1 615 cm^{-1} in their IR spectra. Wave number $v_{as}(N_3)$ at 2 115 cm^{-1} is diagnostic of compound *I*. The $v(NH)$ bands for compounds *II, III, IV, VII, IX, XI, XII* are at 3 480—3 280 cm^{-1}; electron-donating substituents lower the wave number of NH, this being in accord with the literature[15]. Compound *VIII* displayed the $v(C≡N)$ at 2 240 cm^{-1}, compounds *II*—*X* have their $v(C=O)$ vibration bands at 1 605—1 685 cm^{-1}. The UV spectral data show that alkylation at nitrogen atom of benzofuro[3,2-*b*]pyrrole system did not markedly influence the position of λ_{max}. Comparison of λ_{max} of ethyl 2-azido-3-(2-benzofuryl)acrylate (*I*) (348 nm) and ethyl 2-azido-3-(2-furyl)acrylate (294 nm, ref.[4]) showed that the fusion of a benzene ring caused a bathochromic shift. Analogous shifts were also observed with other corresponding compounds.

SCHEME 2

Structure of the synthesized substances was also corroborated by ^1H and ^{13}C NMR spectra. Methylation of the NH group in XI was associated with the change in multiplicity of the $C_{(3)}$—H proton signal from a doublet-doublet to a doublet, thus proving the structure assigment for XII. Comparison of chemical shifts of pairs of compounds II and VI, IX and X, III and VII, and XI and XII showed that methylation in position 1 resulted in an upfield shift of the $C_{(3)}$—H proton signal. Also the kind of substituents in position 2 influenced the chemical shift of the $C_{(3)}$—H proton signal: due to the electronic and anisotropic effects of the carbonyl group this signal was downfield shifted. Table I lists the ^{13}C NMR spectra of compounds II, VI, XI, and XII. Carbon atoms were assigned according to analogy of chemical shift values and coupling constants with those of benzofuran[16] and furo[3,2-b]pyrrole derivatives[4]. The effect of the methyl group at nitrogen was manifested with compounds II and VI by the chemical shift values of carbons of the pyrrole ring, where an upfield shift of carbon atoms 4 and 2 signals and a downfield shift of the $C_{(3)}$ signal were observed.

Molecular ion peaks of compounds VI and XI have the maximum, that of II 76·6% relative intensities. The main fragmentation pattern involves a cleavage of the

Scheme 3

neutral C_2H_5OH molecule (Scheme 2). This fragmentation is analogous to that of ethyl furo[3,2-b]pyrrole-5-carboxylate[4]. The species at m/z 201 originated *via* elimination of the neutral ethylene molecule. This fragmentation pathway also applies to compound *VI* having the methyl group in position 1 (Scheme 3), but the species is of greater intensity.

EXPERIMENTAL

2-Benzofurancarbaldehyde

Phosphorus oxidochloride (230 g, 1·5 mol) was added in small portions to a mixture of benzo-furan (118 g, 1 mol) in dimethylformamide (110 g) at room temperature. The mixture was stirred at 20°C for 1 h and at 50°C for 40 h, poured onto crushed ice (1 kg), the pH adjusted to 6 with a 20% NaOH and extracted with ether. The organic layer was dried with Na_2SO_4, the solvent removed and the residue distilled. Yield 75 g (49%), b.p. 122—124/1·5 kPa; (ref.[17] 135—136°C : : 2·4 kPa).

TABLE I

^{13}C Chemical shifts (δ, ppm) of compounds *II*, *VI*, *XI*, *XII*, (spectra with a heteronuclear ^{13}C—H decoupling)
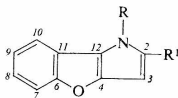
Compound	C_2	C_3	C_4	C_6	C_7	C_8	C_9
II	128·4	97·0	149·3	160·7	112·8	124·6	122·7
VI	128·0	97·8	146·9	160·3	112·5	124·5	122·5
XI	121·4	92·4	150·3	159·2	112·3	122·2	122·2
XII	124·9	90·9	149·7	159·0	112·2	122·1	121·9

	C_{10}	C_{11}	C_{12}	CO	NCH_3	OCH_2	CH_3
II	118·3	118·1	124·4	162·3	—	60·8	14·5
VI	117·6	118·2	124·4	161·7	34·9	60·0	14·4
XI	116·5	119·2	119·7	—	—	—	—
XII	115·9	119·5	121·5	—	35·4	—	—

Ethyl 2-Azido-3-(2-benzofuryl)acrylate (*I*)

A solution of 2-benzofurancarbaldehyde (2·4 g, 16 mmol) and ethyl azidoacetate (10·3 g, 80 mmol) was added at 0°C to a solution of sodium ethoxide prepared from sodium metal (1·84 g, 80 mmol) and ethanol (60 m)l. The mixture was stirred at 10°C for 1 h, cooled and a solution of ammonium chloride (4 h, in water (20 ml) was added. After a 10 min-stirring it was poured into water (400 ml) and the separated *I* filtered off. Yield 2·7 g 64%, m.p. 70°C (methanol), For $C_{13}H_{11}N_3O_3$ (257·3) calculated: 60·70% C, 4·31% H, 16·33% N; found: 60·58% C, 4·28% H, 16·28% N. IR spectrum (CHCl₃), ν_{max} cm^{-1}: 2 115 (N₃); 1 700 (C=O); 1 605 (C=C). UV spectrum λ_{max} nm (log ε): 348 (4·59), 255 (3·90), 233 (3·94), 205 (4·37). ¹H NMR spectrum (CDCl₃): 6·93 (1 H, d, C_A—H), 7·44 (1 H, d, $C_{(3)}$—H), 4·37 (2 H, q, O—CH₂), 1·37 (3 H, t, CH₃), 7·12—7·78 (4 H, m, H_{arom}), $J_{3,A} = 0·5$.

Ethyl Benzofuro[3,2-*b*]pyrrole-2-carboxylate (*II*)

Ester *I* (1 g, 4 mmol) was stirred and heated in boiling toluene (100 ml) for 20 min and the solvent distilled off under diminished pressure. Yield 0·85 (96%), m.p. 166°C (benzene). For $C_{13}H_{11}NO_3$ (229·2) calculated: 68·11% C, 4·84% H, 6·11% N; found: 68·02% C, 4·80% H, 6·26% N. IR spectrum (CHCl₃), ν_{max} cm^{-1}: 3 410 (N—H), 1 685 (C=O), 1 545 (C=C); UV spectrum λ_{max} nm (log ε): 323 (4·63), 318 (4·60), 258 (4·19), 250 (4·18), 217 (4·14). ¹H NMR spectrum (CDCl₃): 6·86 (1 H, d, $C_{(3)}$—H), 4·31 (2 H, q, O—CH₂), 1·37 (3 H, q, CH₃), 10·12 (1 H, bm,, NH), 7·12 to 7·75 (4 H, m, H_{arom}), $J_{1,3} = 1·8$. Mass spectrum, m/z (%): 229 (78·6), 201 (7·2), 183 (100), 156 (15), 128 (6·7).

Benzofuro[3,2-*b*]pyrrole-2-carboxylic Acid Hydrazide (*III*)

Solution of *II* (1 g, 4 mmol) in methanol (50 ml) was refluxed with hydrazine hydrate (3·5 g, 80%) for 40 h anf the solvent was distilled off. Yield 0·74 g (79%), m.p. 239—240°C (methanol). For $C_{11}H_9N_3O_2$ (215·2) calculated: 61·39% C, 4·21% H, 19·52% N; found: 61·42% C, 4·24% H, 19·65% N, IR sp,ctrum (KBr), ν_{max} cm^{-1}: 3 280 (N—H), 1 605 (C=O), 1 555 (C=C). UV spectrum λ_{max} nm, (log ε) 318 (4·51), 250 (4·13), 217 (4·22). ¹H NMR spectrum (hexadeuterio-dimethyl sulfoxide): 6·93 (1 H, s, $C_{(3)}$—H), 7·12—7·87 (4 H, m, H_{arom}), 12·0 (1 H, b, N—H), 9·56 (1 H, b, N—H), 4·47 (2 H, b, NH₂).

1-Methylbenzofuro[3,2-*b*]pyrrole-2-carboxylic acid hydrazide (*VII*) wqs prepared in an analogous way. Yield 0·8 g (83%), m.p. 235°C (methanol). For $C_{12}H_{11}N_3O_2$ (223·2) calculated: 64·57% C, 4·96% H, 18·32% N; found: 64·42% C, 4·90% H, 18·15% N. IR spectrum (KBr), ν_{max} cm^{-1}: 3 220 (N—H), 1 620 (C=O), 1 535 (C=C). UV spectrum λ_{max} nm, (log ε): 318 (4·95), 257 (4·69), 253 (4·70), 221 (4·78). ¹H NMR spectrum (hexadeuteriodimethyl sulfoxide): 6·85 (1 H, s, $C_{(3)}$—H), 4·18 (3 H, t, CH₃), 9·37 (1 H, b, N—H), 4·37 (2 H, b, NH₂), 7·12—8·00 (4 H, m, H_{arom}).

2H-Dihydrobenzofuro[2′,3′-4,5]pyrrole[1,2-*d*]1,2,4-triazin-1-one (*IV*)

The hydrazide *III* (2·15 g, 10 mmol) and ethyl orthoformate (2 g, 14 mmol) were dissolved in dimethylformamide (10 ml) and refluxed for 2·5 h. The solvent was removed *in vacuo* and the residue crystallized. Yield 1·2 g (58%), m.p. 330—331°C (dimethylformamide). For $C_{12}H_7N_3O_2$ (225·2) calculated: 64·00% C, 3·13% H, 18·66% N; found: 64·12% C, 3·20% H, 18·59% N. IR IR spectrum (KBr), ν_{max} cm^{-1}: 3 170 (N—H), 1 660 (C=O), 1 545 (C=C). ₐV spectrum λ_{max} nm, (log ε): 321 (4·59), 309 (4·54), 278 (4·19), 244 (4·67), 219 (4·29). ¹H NMR spectrum (hexadeuterio-dimethyl sulfoxide): 7·25 (1 H, d, $C_{(11)}$—H), 9·14 (1 H, d, $C_{(4)}$—H), 7·37—8·36 (4 H, m, H_{arom}), $J_{4,11} = 0·8$.

2*H*-Dihydro-4-methylbenzofuro[2′,3′-4,5]pyrrolo[1,2-*d*]-1,2,4-triazin-1-one (*V*)

The hydrazide *III* (2·15 g, 10 mmol) and ethyl orthoacetate (2 g, 12 mmol) were hot-dissolved in dimethylformamide (10 ml), refluxed for 2·5 h and the solvent distilled off under reduced pressure. Yield 2·2 g (94%), m.p. 308°C (dimethylformamide). For $C_{13}H_9N_3O_2$ (239·2) calculated: 65·27% C, 3·79% H, 17·56% N; found: 65·85% C, 3·84% H, 17·69% N. IR spectrum (KBr), v_{max} cm^{-1}: 3 150 (N—H), 1 660 (C=O), 1 540 (C=C). UV spectrum λ_{max} nm, (log ε): 326 (4·59), 310 (4·56), 281 (4·11), 242 (4·61), 236 (4·60), 220 (4·31). ^{1}H NMR spectrum (hexadeuteriodimethyl sulfoxide): 7·19 (1 H, s, $C_{(11)}$—H), 2·91 (3 H, s, CH$_3$). 7·37—8·36 (4 H, d, H$_{arom}$).

Ethyl 1-Methylbenzofuro[3,2-*b*]pyrrole-2-carboxylate (*VI*)

To the solution of the ester *II* (1·16 g, 5 mmol) in benzene (100 ml) NaOH (30 ml, 50%) was added and the two-phase solution treated with stirring with methyl iodide (1 g, 7 mmol) and triethylammonium bromide (0·4 g). The solution was stirred at 65°C for 4 h, cooled, the organic layer separated and the aqueous one extracted with ether. The combined extracts were washed with water, dried with Na$_2$SO$_4$ and the solvent removed under diminished pressure. Yield 0·8 g (72%), m.p. 114—115°C (ethanol). For $C_{14}H_{13}NO_3$ (243·2) calculated: 69·13% C, 5·38% H, 5·76% N; found: 69·20% C, 5·36% H, 5·69% N. IR spectrum (CHCl$_3$), v_{max} cm^{-1}: 2 940 (C—H), 1 683 (C=O), 1 525 (C=C). UV spectrum λ_{max} nm, (log ε): 323 (4·63), 314 (4·61), 262 (4·15), 254 (4·11), 222 (4·10). ^{1}H NMR spectrum (CDCl$_3$): 6·83 (1 H, s, $C_{(3)}$—H), 4·18 3 H, s, N—CH$_3$); 7·12—8·0 (4 H, m, H$_{arom}$). Mass spectrum, m/z (%): 243 (100), 215 (74·6), 198 (5·4), 172 (6·2), 169 (7·5), 115 (14·9).

Ethyl 1-(2-Cyanoethyl)benzofuro[3,2-*b*]pyrrole-2-carboxylate (*VIII*)

To the ester *II* (1 g, 4 mmol) dissolved in pyridine (10 ml) acrylonitrile (1·5 g, 30 mmol) and triethylbenzylammonium hydroxide (0·5 mmol) were added and the mixture heated at the boiling temperature for 15—20 min. Work-up in the usual way yielded 0·3 g (28%) of the product, m.p. 117—118°C (ethanol). For $C_{16}H_{14}N_2O_3$ (282·3) calculated: 68·08% C, 5·00% H, 9·92% N; found: 67·92% C, 5·10% H, 9·88% N. IR spectrum (CHCl$_3$), v_{max} cm^{-1}: 2 240 (CN), 1 685 (C=O), 1 530 (C=C). UV spectrum λ_{max} nm, (log ε): 325 (4·62), 321 (4·62), 260 (4·20), 252 (4·17), 220 (4·13). ^{1}H NMR spectrum (CDCl$_3$): 6·90 (1 H, s, $C_{(3)}$—H), 4·85 (2 H, t, N—CH$_2$), 2·96 (2 H, t, CH$_2$—C=N), 4·31 (2 H, q, O—CH$_2$), 1·37 (3 H, t, CH$_3$), 6·12—7·75 (4 H, m, H$_{arom}$).

Benzofuro[3,2-*b*]pyrrole-2-carboxylic Acid (*IX*)

Sodium hydroxide (30 ml, 5%) was added to the solution of the ester *II* (2·29 g, 10 mmol) in ethanol (100 ml). The solution was refluxed for 2 h, the separated sodium salt dissolved in ethanol—water 1 : 1, heated with charcoal, filtered, cooled and precipitated by addition of HCl to a weak acid reaction. The separated crystals were filtered off and washed with water. Yield 1·8 g (89%), m.p. 234°C (ethyl acetate). For $C_{11}H_7NO_3$ (201·2) calculated: 65·67% C, 3·51% H, 6·96% N; found: 65·58% C, 3·24% H, 7·07% N. IR spectrum (KBr), v_{max} cm^{-1}: 3 400 (N—H), 1 660 (C=O) 1 550 (C=C). UV spectrum λ_{max} nm, (log ε): 317 (4·68), 311 (4·57)%, 253 (4·21), 250 (4·22), 214 (4·18). ^{1}H NMR spectrum (hexadeuteriodimethyl sulfoxide): 6·81 (1 H, s, $C_{(3)}$—H), 7·26 to 7·78 (4 H, m, H$_{arom}$), pK_A 6·34.

1-Methylbenzofuro[3,2-*b*]pyrrole-2-carboxylic acid (*X*) was prepared analogously. Yield 1·9 g (87%), m.p. 220—221°C (ethyl acetate). For $C_{12}H_9NO_2$ (215·2) calculated: 66·07% C, 4·21% H, 6·50% N; found: 66·87% C, 4·18% H, 6·56% N. IR spectrum (KBr), v_{max} cm^{-1}:

1 680 (C=O), 1 530 (C=C). UV spectrum λ_{max} nm, (log ε): 318 (5·53), 307 (4·49), 261 (4·10), 257 (3·11), 252 (4·12), 218 (4·09). ^{1}H NMR spectrum (hexadeuteriodimethyl sulfoxide): 6·87 (1 H, s, C$_{(3)}$—H), 7·30—7·80 (4 H, m, H$_{arom}$), 4·21 (3 H, s, CH$_3$), pK_A: 6·57.

Benzofuro[3,2-*b*]pyrrole (*XI*)

A mixture consisting of acid *IX* (2·01 g, 10 mmol) and copper(II) chromite (0·64 g) in quinoline (20 ml) was stirred in a nitrogen atmosphere. The temperature was raised to 120 — 122°C and kept constant untill the formation of carbon dioxide ceased (checked by calcium hydroxide solution), and then ether (300 m)l was added to the cooled solution. The etheral solution was washed with 0·1M-HCl (approx. 3 000 ml) and water (approx. 600 ml), dried with Na$_2$SO$_4$ and the solvent distilled off. Yield 0·7 g (43%), m.p. 86°C (ether–hexane 1 : 5). For C$_{10}$H$_7$NO (157·2) calculated: 76·42% C, 4·49% H, 8·9% N; found: 76·40% C, 4·45% H, 9·07% N. IR spectrum (CHCl$_3$), ν_{max} cm^{-1}: 3·480 (N—H), 1 610 (C=C). UV spectrum λ_{max} nm, (log ε): 296 (4·32), 278 (4·55), 243 (4·46), 218 (4·45). ^{1}H NMR spectrum (CDCl$_3$): 6·75 (1 H, dd, C$_{(2)}$—H), 6·22 (1 H, dd, C$_{(3)}$—H), 7·06—7·62 (4 H, m, H$_{arom}$), 7·95 (1 H, m, NH), $J_{2,3} = 3\cdot1$, $J_{1,3} = 1\cdot8$, $J_{1,2} = 3\cdot1$. Mass spectrum m/z (%): 157 (100), 156 (7·7), 130 (12·8).

1-Methylbenzofuro[3,2-*b*]pyrrole (*XII*) was prepared analogously at 150—155°C. Yield 0·8 g (47%), m.p. 56—57°C (ether–hexane 1 : 5). For C$_{11}$H$_9$NO (171·2) calculated: 77·17% C, 5·29% H, 8·18% N; found: 77·20% C, 5·30% H, 8·39% N, IR spectrum (KBr), ν_{max} cm^{-1}, 1 615 (C=C). UV spectrum λ_{max} nm, (log ε): 296 (4·14), 278 (4·34), 244 (4·25), 218 (4·20), ^{1}H NMR spectrum (CDCl$_3$): 6·61 (1 H, d, C$_{(2)}$—H), 6·10 (1 H, d, C$_{(3)}$—H), 2·62 (3 H, s, CH$_3$): 7·12—7·88 (4 H, m, H$_{arom}$), $J_{2,3} = 3\cdot1$.

2-Methylbenzofuro[3,2-*b*]pyrrole (*XIII*)

Ester *II* (1·15 g, 5 mmol) in ether (100 ml) was added to a suspension of lithium hydridoaluminate (0·9 g) in ether (30 ml) at an ambient temperature and stirred and refluxed for 90 min. The mixture cooled to 0°C was treated with ethyl acetate, water and sodium hydroxide in order to decompose the excess of hydridoaluminate. The ethereal layer was separated and the aqueous one extracted with ether.The combined extracts was washed with water and dried with Na$_2$SO$_4$, and the solvent evaporated *in vacuo*. Yield 0·7 g (81%), m.p. 132—133°C (ether–hexane 1 : 4). For C$_{11}$H$_9$NO (171·2) calculated: 77·7% C, 5·29% H, 8·18% N; found: 77·87% C, 5·24% H, 8·28% N. IR spectrum (CHCl$_3$), ν_{max} cm^{-1}: 3 470 (N—H), 1 415 (C=C). UV spectrum λ_{max} nm, (log ε): 301 (4·16), 281 (4·33), 242 (4·21), 217 (4·18). ^{1}H NMR spectrum (CDCl$_3$): 5·95 (1 H, bs, C$_{(3)}$—H), 2·35 (3 H, s, CH$_3$), 7·00—7·87 (4 H, m, H$_{arom}$).

1-Methyl-2-hydroxymethylbenzofuro[3,2-*b*]pyrrole (*XIV*) was obtained in an analogous way. Yield 0·7 g (74%), m.p. 156°C (ether). For C$_{12}$H$_{11}$NO$_2$ (202·2) calculated: 71·28% C, 5·48% H, 6·93% N; found: 71·18% C, 5·42% H, 7·18% N. IR spectrum (KBr), ν_{max} cm^{-1}: 3 190 (OH), 1 615 (C=C). UV spectrum λ_{max} nm, (log ε): 297 (4·27), 283 (4·37), 247 (4·27), 216 (4·15). ^{1}H NMR spectrum (hexadeuteriodimethyl sulfoxide): 6·11 (1 H, s, C$_{(3)}$—H), 4·53 (2 H, d, CH$_2$), 5·15 (1 H, t, OH), 3·86 (3 H, s, CH$_3$), 7·00—7·75 (4 H, m, H$_{arom}$), $J_{CH_2OH} = 4\cdot9$.

Spectral Measurements

Infrared spectra were measured with a Specord 71 IR (Zeiss, Jena), ultraviolet spectra of 2 . . $10^{-5} - 5 . 10^{-5}$ mol l^{-1} methanolic solutions in the 200—800 nm range with a Specord UV VIS (Zeiss, Jena) apparatuses. The ^{1}H NMR spectra were recorded with a Tesla BS 487 C spectrometer operating at 80 MHz values at δ scale in ppm). The internal standards were hexa-

methyldisiloxane and tetramethylsilane for hexadeuteriodimethyl sulfoxide and deuteriochloroform solutions, respectively. The ^{13}C NMR spectra of compounds *II*, *IV*, *V*, and *VII* were run in deuteriochloroform with a Jeol FX-100 spectrometer operating at 25·04 MHz. The electron impact mass spectra of substances *II*, *VI*, and *XI* were measured with an MS 902 S (AEI Manchester) apparatus at an ionizing electron energy 70 eV, trap current 100 μA and the ionization chamber temperature 80°C. Peaks of relative intensity $\leqq 5$ were omitted.

Determination of pK_A Values

Potentiograph E 436 (Metrohm, Switzerland) was used for measurements; the glass electrode was calibrated by a standard aqueous solution.

Hydrochloric acid (0·1M) in dioxane–water (1 : 1) was added to sodium salt of the acid (20 ml, 5 mmol l^{-1}) in an inert atmosphere. The procedure according to[18] was employed for calculation of the pK_A values.

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