ADDITION AND CYCLOADDITION REACTIONS OF FURO[3,2-*b*]-PYRROLES AND THEIR BENZO[*b*] ANALOGUES: AN NMR STUDY OF STRUCTURE OF PRODUCTS

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Received August 19th, 1987
Accepted December 13th, 1987

Reaction of furo[3,2-*b*]pyrroles and their benzo[*b*] analogues with dimethyl butynedioate and ethyl propynoate were investigated. The reaction course is influenced by substituents on the system. Products of [4 + 2] cycloaddition to the furan or pyrrole nucleus as well as products of Michael addition to the benzo[*b*]furo[3,2-*b*]pyrrole system have been found. The structure of the products has been proven by ^{1}H NMR and ^{13}C NMR spectroscopy.

In our previous studies we investigated addition and cycloaddition reactions of substituted furo[3,2-*b*]pyrroles. We described[1] the 1,3-dipolar cycloadditions of two furo[3,2-*b*]pyrrole derivatives with C-benzoyl-N-phenylnitrone and N,N-diphenylnitrone which proceeded regiospecifically in positions 2 and 3 of the furan nucleus. In another paper[2] we have published the results of studies on the reaction of 2-aryl-4*H*-furo[3,2-*b*]pyrroles and their N-substituted derivatives with dimethyl butynedioate. Depending on the substituent in position 4 of the furo[3,2-*b*]pyrrole system, the reaction afforded products of Michael addition or [4 + 2] cycloaddition with subsequent transformation of the pyrrole ring leading to substituted benzo[*b*]furan derivatives.

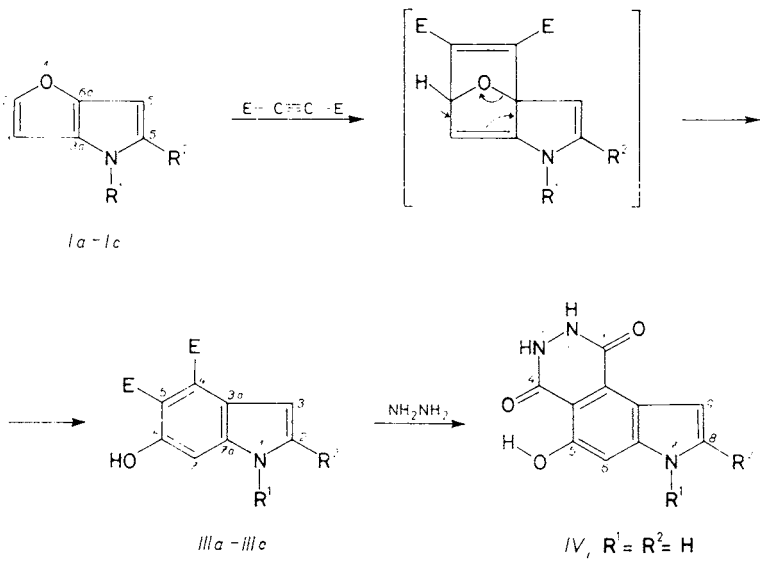
As a continuation of our previous studies we tried to get a deeper insight into the reactivity of furo[3,2-*b*]pyrroles by investigation of reactions of further variously substituted types with dienophiles. Addition reactions of furo[3,2-*b*]pyrrole and its derivatives have not been studied so far. It was of interest whether this system will retain the properties of furan and pyrrole, from which it has formally arisen, or will behave as its isoelectronic analogue, indole.

As known, pyrroles and indoles undergo Michael addition with π-deficient alkenes and alkynes in position 2 of the pyrrole ring and in position 3 of the indole ring, but also on the NH group. Under catalysis with Lewis acids, and particularly at elevated temperatures, [4 + 2] cycloaddition reactions take place[3-6]. With dieno-

philes, furan and its derivatives afford mainly cycloaddition products[7]; however, also products of addition in α-position of the furan ring were isolated[8].

Our present study concerns reactions of 4*H*-furo[3,2-*b*]pyrrole (*Ia*), its 4-acetyl (*Ib*), and 5-ethoxycarbonyl (*Ic*) derivatives, as well as benzo[*b*]furo[3,2-*b*]pyrrole (*IIa*) and its 1-methyl (*IIb*) and 1-acetyl (*IIc*) derivatives, with dimethyl butynedioate.

Our investigations have shown that with furo[3,2-*b*]pyrrole derivatives containing no substituent in position 2 the cycloaddition reaction proceeds on the furan nucleus, giving rise to substituted indoles (Scheme 1). The reaction was used for preparation



In formulae *I* and *III*: *a*, $R^1 = R^2 = H$; *b*, $R^1 = COCH_3$, $R^2 = H$; *c*, $R^1 = H$, $R^2 = COOC_2H_5$;

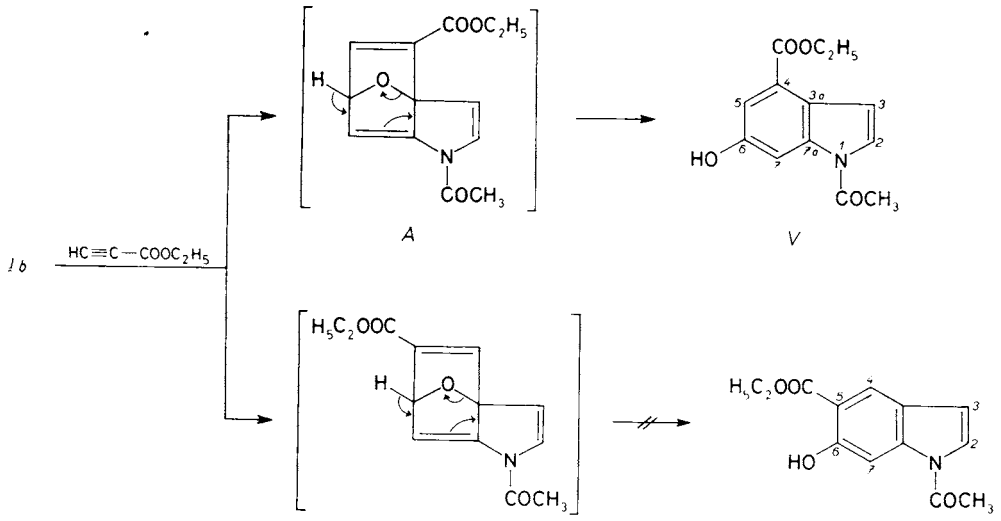
$E = COOCH_3$

SCHEME 1

of substituted 6-hydroxy-4,5-indoledicarboxylates *IIIa*, *IIIb* or 2,4,5-tricarboxylate *IIIc* starting from compounds *I*. Compound *IIIa* reacted with hydrazine hydrate to give the new compound *IV*, containing the pyridazino[4,5-*e*]indole grouping.

For the study of reaction with unsymmetrically substituted dienophiles we used ethyl propynoate and 4-acetylfuro[3,2-*b*]pyrrole (*Ib*). In principle, this reaction can afford two stereoisomeric 1 : 1 adducts which on subsequent rearrangement give isomeric 1-acetylindole derivatives (Scheme 2).

As shown by ^1H NMR spectra of the crude product, the reaction under the given conditions proceeds regioselectively to afford ethyl 1-acetyl-6-hydroxy-4-indolecarboxylate (*V*) without any side products other than bituminous unidentified material.

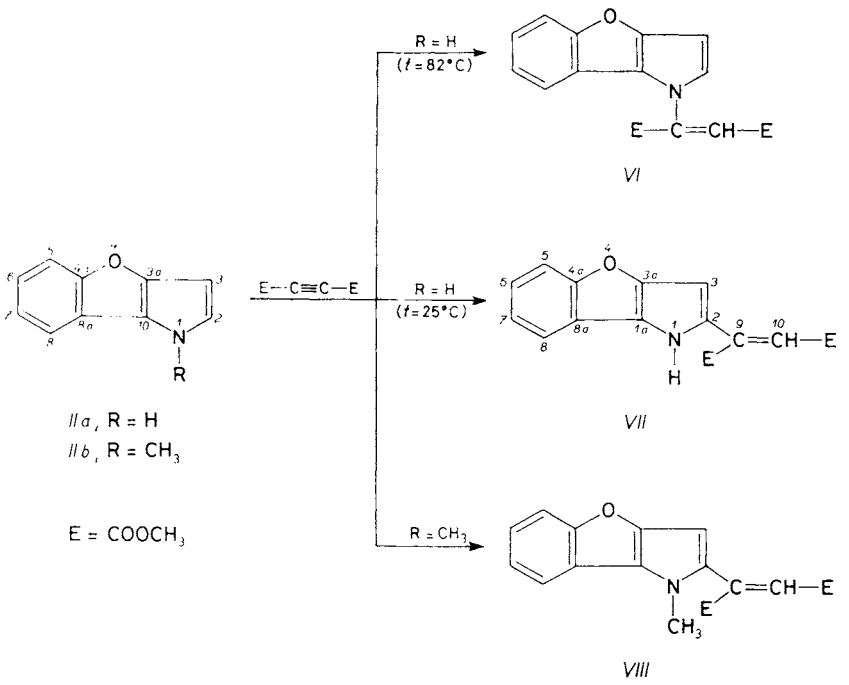


SCHEME 2

The fact that the reaction rate increases with increasing solvent polarity indicates that the formation of the tricyclic intermediate *A* is not a concerted process but proceeds in two separate steps of which the first one starts by an attack by the more electrophilic centre of the dienophile at the more reactive position C-2 of the furan nucleus, in accord with the results obtained by us in the investigation of substitution reactions of furo[3,2-*b*]pyrrole derivatives[9]. In the second step, the formed carbanion attacks the carbon atom common to both rings. The arising (undetected) cycloadduct is obviously labile and is transformed by opening of the furan ring into the indole derivative.

Reaction of benzo[*b*]furo[3,2-*b*]pyrrole (*IIa*) with dimethyl butynedioate afforded only the Michael addition products *VI* and *VII*. When the reaction was performed in acetonitrile at room temperature, only the 2-addition product *VII* was obtained; on the other hand, in boiling acetonitrile the 1-addition product *VI* was isolated. 1-Methylbenzo[*b*]furo[3,2-*b*]pyrrole (*IIb*) furnished the Michael-type adduct *VIII* (addition at C-2) as the sole product (Scheme 3).

Concerning the reaction of 1-acetylbenzo[*b*]furo[3,2-*b*]pyrrole (*IIc*) we assumed that mesomeric conjugation of the acetyl group with the π-electron system of the skeleton leads to partial localization of the lone electron pair at the nitrogen atom enhancing thus the diene character of its pyrrole part. This assumption has been confirmed by isolation of dimethyl 3-acetylaminodibenzofuran-1,2-dicarboxylate (*IX*) as product of the very slow reaction. The structure *IX* was also confirmed

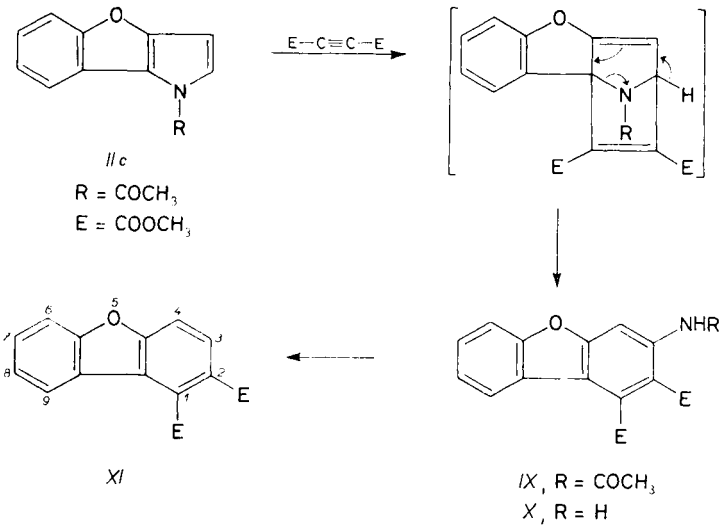


SCHEME 3

chemically (Scheme 4) by independent preparation[10] of compound *XI* from dimethyl butynedioate and 2-vinylbenzo[*b*]furan.

We have found that the reactivity toward dienophiles in both the studied series is influenced by substituents. The furo[3,2-*b*]pyrrole series is more reactive and the cycloaddition takes place at the furan nucleus. When the C-2 position is substituted, the reaction proceeds on the pyrrole nucleus and is more facile than in the benzo[*b*]-furo[3,2-*b*]pyrrole series. One can say that in fused furo[3,2-*b*]pyrrole systems each nucleus retains its original identity and the reactivity increases on going from pyrrole to furan, i.e. as in non-fused systems.

The structure of the final products of the studied reactions has been confirmed by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H and ^{13}C NMR data are given in the experimental part. The reaction product from 4-acetylfuro[3,2-*b*]pyrrole (*Ib*) with dimethyl butynedioate was assigned the structure *IIIb* using the FT NMR techniques described in ref.[11]. The measurement of connectivity of carbon atoms 7–6–5 by the 1D-INADEQUATE method has confirmed the position of the hydroxyl group and has shown that the reaction afforded dimethyl 1-acetyl-6-hydroxy-4,5-indoledicarboxylate (*IIIb*) according to Scheme 1.



IIc

XI

IX, R = $COCH_3$
X, R = H

SCHEME 4

The structure of compounds *IIIa* and *IIIc* was confirmed by ^{1}H NMR spectra and their comparison with compound *IIIb* whose structure had been unequivocally established[11]. In addition to their coupling (J(2, 3) = 3·8 Hz), the signals of protons H-2 and H-3 in *IIIa* are split by the indole NH proton, in compound *IIIc* the H-3 signal is split by the NH proton. In both *IIIa* and *IIIc* there is a long-range coupling between the H-3 and H-7 protons, ^5J(3, 7) = 0·7–1·0 Hz. The position of the OH signal was determined by deuteration with deuterium oxide. Compared with compounds *IIIa* and *IIIc*, the H-7 signal in *IIIb* is shifted ($\Delta\delta$ = 1·21 and 1·14ppm, respectively) as the result of anisotropy of the N-acetyl group. The experimentally determined chemical shifts of the H-7 proton signals for *IIIa* and *IIIc* (δ 6·91 and 6·98, respectively) agree with the value δ = 7·16 calculated using increments for an aromatic system and confirm the position of the substituents on the benzene ring of the indole skeleton. The signals of protons in 1-acetyl-6-hydroxy-4-indolecarboxylate (*V*) were assigned on the basis of the J(H, H) coupling constants. The H-2 signal appears as a doublet with coupling constant J(2, 3) = 3·8 Hz, the H-3 signal forms a doublet of doublets resulting from a long-range coupling with H-7 (J(3, 7) = = 0·7 Hz). The position of substituents on the benzene ring in *V* is unequivocally confirmed by the coupling constant J(5, 7) = 2·2 Hz, characteristic of coupling of *meta*-protons. Assignment of signals in the ^{13}C NMR spectra was done on the basis of characteristic splitting caused by long-range coupling and was confirmed by selective heteronuclear decoupling. For assignment of quaternary carbon atoms the selective IERPT technique was applied, analogously as described in our previous paper[11].

The structure of the final products arising in reaction of benzo[*b*]furo[3,2-*b*]pyrrole derivatives *IIa*–*IIc* with dimethyl butynedioate has been confirmed by the ^{1}H and ^{13}C NMR spectra. The Michael addition products *VI*–*VIII* were proven by the signal of the olefinic proton H-10 and of the proton H-3 in compounds *VII* and *VIII*; in *VII* the H-3 signal is split into a doublet due to the coupling with the NH proton. The spectrum of *VI* displays doublets of H-2 and H-3 protons with coupling constant $J(2, 3) = 3{\cdot}2$ Hz. The large chemical shift of the N—H signal (δ 12·92) in the spectrum of *VII* indicates an intramolecular hydrogen bond between the NH proton and the methoxycarbonyl group at the C-9 carbon atom. The position of the signal does not change with concentration of the solution.In the unsubstituted benzo[*b*]furo[3,2-*b*]pyrrole the NH proton signal appears at δ 7·95 (ref.[12]). The signals of the carbon atoms in the ^{13}C NMR spectra have been assigned on the basis of analogy with the chemical shifts and coupling constants J(C, H) in the proton-coupled spectra of some substituted benzo[*b*]furo[3,2-*b*]pyrrole derivatives[12]. The value of the vicinal coupling constant ^3J(CO, H-10) (10·6 Hz) for the derivative *VIII* confirmed the *Z*-configuration of the side-chain double bond.

Reaction of 1-acetylbenzo[*b*]furo[3,2-*b*]pyrrole (*IIc*) with dimethyl butynedioate gave dimethyl 3-acetylaminodibenzofuran-1,2-dicarboxylate (*IX*) as confirmed by ^{1}H NMR parameters. The structure of the product was also proven by deacetylation, followed by deamination to the known[10] ester *XI* (Scheme 4).

The ^{1}H NMR spectra of the cycloaddition product *XI* exhibit two doublets of the H-3 and H-4 protons at δ 8·10 and δ 7·89 with coupling constant $J(3, 4) = 8{\cdot}7$ Hz, characteristic of coupling between two protons in *o*-position, proving thus its structure.

EXPERIMENTAL

Infrared spectra were recorded on a Specord 71 IR, UV spectra on a Specord UV VIS (Zeiss, Jena) spectrophotometers at concentrations $1 \cdot 10^{-5}$–$5 \cdot 10^{-5}$ mol dm^{-3}. ^{1}H NMR spectra were measured on an 80 MHz BS 487C Tesla spectrometer with tetramethylsilane and hexamethyldisiloxane as internal standards in deuteriochloroform and hexadeuteriodimethyl sulfoxide, respectively. ^{13}C NMR spectra were taken on a Bruker AM-300 instrument at 75·43 MHz. Mass spectra were obtained with an MS 902S (AEI, Manchester) spectrometer (direct inlet, electron energy 70 eV, trap current 100 μA, ionization chamber temperature 80°C).

The starting compounds were prepared as described: *Ib* and *IIc* (ref.[13]), *Ic* (ref.[14]), *IIa* and *IIb* (ref.[12]).

4*H*-Furo[3,2-*b*]pyrrole (*Ia*)

A solution of 4-acetylfuro[3,2-*b*]pyrrole (1·00 g; 6·7 mmol) in ethanol (25 ml) was refluxed with 5% sodium hydroxide solution (15 ml) for 20 min and poured on ice. Extraction with ether, washing the extract with 0·1M-HCl and water, drying over sodium sulfate and evaporation of the solvent afforded *Ia* (0·50 g; 70%), m.p. 39°C (diethyl ether–hexane 1 : 1) (reported[15] m.p. 39°C). ^{1}H NMR (CD_3SOCD_3): 7·42 dd, 1 H (H-2); 6·50 dd, 1 H (H-3); 6·78 dd, 1 H (H-5);

6·04 dd, 1 H (H-6); 10·46 bs (H-4); $J(2, 3) = 2·2$, $J(2, 5) = 1·3$, $J(5, 6) = 3·0$, $J(3, 6) = 0·8$, $J(4, 5) = 3·0$, $J(4, 6) = 1·6$ Hz. ^{13}C NMR (CD_3SOCD_3): 144·11 (C-2); 99·63 (C-3); 120·77 (C-5); 90·61 (C-6); 148·07 (C-6a); 123·90 (C-3a).

Dimethyl 6-Hydroxy-4,5-indoledicarboxylate (*IIIa*)

A mixture of 4*H*-furo[3,2-*b*]pyrrole (0·53 g; 5 mmol), dimethyl butynedioate (0·80 g; 5·6 mmol) and acetonitrile (8 ml) was refluxed for 1 h. After evaporation of the solvent in vacuo the residue was extracted with ether, the ethereal solution was concentrated, light petroleum was added and the product was collected on a filter; yield 0·25 g (40%), m.p. 109°C (ether–light petroleum). For $C_{12}H_{11}NO_5$ (249·2) calculated: 57·83% C, 4·46% H, 5·62% N; found: 57·56% C, 4·48% H, 5·73% N. IR spectrum (KBr), cm^{-1}: 1 710 (C=O). ^{1}H NMR ($CDCl_3$): 7·05 dd, 1 H (H-2); 6·39 m, 1 H (H-3); 6·91 d, 1 H (H-7); 10·58 s, 1 H (OH); 8·65 bs, 1 H (H-1); 3·91 s, 3 H ($COOCH_3$); 3·97 s, 3 H ($COOCH_3$); $J(2, 3) = 3·5$, $J(1, 2) = 2·2$, $J(1, 3) = 1·8$ Hz, $J(3, 7) = 0·8$ Hz.

Dimethyl 1-Acetyl-6-hydroxy-4,5-indoledicarboxylate (*IIIb*)

A mixture of 4-acetylfuro[3,2-*b*]pyrrole (1·00 g; 6·7 mmol), dimethyl butynedioate (1·08 g; 7·6 mmol) and acetonitrile (20 ml) was refluxed for 16 h, The separated white crystalline compound was collected, yield 1·50 g (77%), m.p. 206°C (methanol). For $C_{14}H_{13}NO_6$ (291·3) calculated: 57·73% C, 4·50% H, 4·81% N; found: 57·83% C, 4·49% H, 4·98% N. IR spectrum (KBr), cm^{-1}: 1 720, 1 655 (C=O). UV spectrum λ_{max}, nm (log ε, m^2 mol^{-1}): 246 (3·44). ^{1}H NMR ($CDCl_3$): 7·38 d, 1 H (H-2); 6·48 dd, 1 H (H-3); 8·12 d, 1 H (H-7); 10·62 s, 1 H (OH); 3·96 s, 3 H ($COOCH_3$); 3·94 s, 3 H ($COOCH_3$); 2·60 s, 3 H ($NCOCH_3$). ^{13}C NMR (CD_3SOCD_3): 128·09 (C-2); 107·99 (C-3); 120·02 (C-4); 119·91 (C-5); 152·43 (C-6); 107·02 (C-7); 136·34 (C-7a); 121·99 (C-3a); 167·42 ($COOCH_3$); 165·79 ($COOCH_3$); 169·96 (N—$COCH_3$); 52·45 ($COOCH_3$); 52·17 ($COOCH_3$); 23·79 (N—$COCH_3$). Mass spectrum, *m/z* (%): 291 (36), 259 (48·7), 249 (12·8), 217 (100), 159 (71·8), 131 (188), 43 (25·6)t 28 (25·6).

Dimethyl 2-Ethoxycarbonyl-6-hydroxy-4,5-indoledicarboxylate (*IIIc*)

A mixture of ethyl 4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (3·58 g; 20 mmol), dimethyl butynedioate (3·55 g; 25 mmol) and acetonitrile (25 ml) was refluxed for 2 weeks. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel in benzene to give 3·85 g (60%) of *IIIc*, m.p. 179–181°C (benzene). For $C_{15}H_{15}NO_7$ (321·3) calculated: 56·04% C, 4·70% H, 4·35% N; found: 56·08% C, 4·78% H, 4·50% N. ^{1}H NMR ($CDCl_3$): 7·11 dd, 1 H (H-3); 6·98 d, 1 H (H-7); 10·60 s, 1 H (OH); 9·41 bs, 1 H (H-1); 3·98 s, 3 H ($COOCH_3$); 3·93 s, 3 H ($COOCH_3$). ^{1}H NMR (CD_3SOCD_3): 7·34 d, 1 H (H-3); 7·20 s, 1 H (H-7); 10·15 s, 1 H (OH); 11·90 bs, 1 H (H-1); 3·76 s, 3 H ($COOCH_3$); 3·88 s, 3 H ($COOCH_3$); $J(3, 7) = 1·0$; $J(1, 3) = 2·1$ Hz.

5-Hydroxy-1,2,3,4-tetrahydropyridazino[4,5-*e*]indole-1,4-dione (*IV*)

A mixture of compound *IIIa* (1·45 g; 5 mmol), 80% hydrazine hydrate (2·00 g) and ethanol (25 ml) was refluxed for 5 h. The grey-brown crystals, separating during the reaction, were collected after cooling; yield 0·76 g (70%) of *IV*, m.p. above 340°C (decomp.). For $C_{10}H_7N_3O_3$ (217·2) calculated: 55·3% C, 3·25% H, 19·35% N; found: 55·3% C, 3·41% H, 19·35% N. ^{1}H NMR (CD_3SOCD_3): 7·45 dd, 1 H (H-8); 7·22 m, 1 H (H-9); 7·18 d, 1 H (H-6); 12·80 bs, 1 H (OH); 11·50 bs, 2 H (H-2, H-3); 8·00 bs, 1 H (H-7); $J(8, 9) = 3·2$; $J(9, 6) = 0·8$; $J(7, 8) = 2·2$ Hz.

Ethyl 1-Acetyl-6-hydroxy-4-indolecarboxylate (*V*)

A mixture of 4-acetylfuro[3,2-*b*]pyrrole (1·49 g; 10 mmol), ethyl propynoate (1·08 g; 11 mmol) and acetonitrile (20 ml) was refluxed for 32 h and the separated white crystals were collected; yield 1·73 g (70%) of compound *V*, m.p. 193–196°C (ethanol). For $C_{13}H_{13}NO_4$ (247·2) calculated: 63·15% C, 5·30% H, 5·66% N; found: 63·20% C, 5·60% H, 5·85% N. ^{1}H NMR (CD_3SOCD_3) 7·77 d, 1 H (H-2); 7·05 dd, 1 H (H-3); 8·12 dd, 1 H (H-7); 7·40 d, 1 H (H-5); 9·80 s, 1 H (OH); 2·62 s, 3 H ($NCOCH_3$); 4·35 q, 2 H (OCH_2); 1·35 t, 3 H (CH_3); $J(2, 3) = 3·8$; $J(3, 7) = 0·7$; $J(5, 7) = 2·2$ Hz. ^{13}C NMR (CD_3SOCD_3): 126·28 (C-2); 108·56 (C-3); 122·24 (C-4); 114·53 (C-5); 155·57 (C-6); 107·64 (C-7); 137·29 (C-7a); 123·17 (C-3a); 166·03 ($COOC_2H_5$); 169·32 ($N—COCH_3$); 60·55 (OCH_2); 13·99 ($—CH_2—CH_3$); 23·21 ($N—COCH_3$). Mass spectrum, *m/z* (%): 247 (67·5), 205 (100), 177 (59·5), 160 (45·9), 133 (27), 104 (18), 76 (11), 43 (35), 28 (49).

Dimethyl Benzo[*b*]furo[3,2-*b*]-1-pyrrolylbutenedioate (*VI*)

A solution of benzo[*b*]furo[3,2-*b*]pyrrole (1·57 g; 10 mmol) and dimethyl butynedioate (1·70 g; 12 mmol) in acetonitrile (20 ml) was refluxed for 2 weeks. The solvent was distilled off, the brown-black residue was mixed with methanol and the green-black crystals were filtered. Chromatography on alumina in ethanol–hexane afforded yellow-green crystals of *VI*, m.p. 97–98°C (ethanol–hexane 1 : 1); yield 0·98 g (33%). For $C_{16}H_{13}NO_5$ (299·3) calculated: 64·21% C, 4·38% H, 4·68% N; found: 64·28% C, 4·30% H, 4·48% N. ^{1}H NMR ($CDCl_3$): 6·84 d, 1 H (H-2); 6·37, 1 H (H-3); 6·96 s, 1 H (H-10); 7·12–7·70 m, 4 H (H-5, H-6, H-7, H-8); 3·85 s, 3 H ($COOCH_3$); 3·53 s, 3 H ($COOCH_3$); $J(2, 3) = 3·2$ Hz. ^{13}C NMR ($CDCl_3$): 126·2 (C-2); 95·2 (C-3); 150·3 (C-3a); 158·9 (C-4a); 116·4 (C-5); 122·4 (C-6); 121·8 (C-7); 122·5 (C-8); 119·1 (C-8a); 121·8 (C-1a); 163·7 ($COOCH_3$); 163·5 ($COOCH_3$); 137·4 (C-9); 112·4 (C-10); 52·1, 53·6 (OCH_3).

Dimethyl Benzo[*b*]furo[3,2-*b*]-2-pyrrolylbutenedioate (*VII*)

A solution of benzo[*b*]furo[3,2-*b*]pyrrole (1·57 g; 10 mmol) and dimethyl butynedioate (1·70 g; 11 mmol) in acetonitrile (20 ml) was stirred at room temperature for 2 weeks. The solvent was distilled off, the residue was mixed with methanol (10 ml) and the dark brown precipitate was crystallized from methanol to give 1·14 g (38%) of *VII* as yellow crystals, m.p. 132°C (methanol). For $C_{16}H_{13}NO_5$ (299·3) calculated: 64·21% C, 4·38% H, 4·68% N; found: 64·32% C, 4·28% H, 4·42% N. ^{1}H NMR ($CDCl_3$): 6·65 d, 1 H (H-3), 6·10 s, 1 H (H-10); 7·20–7·80 m, 4 H (H-5, H-6, H-7, H-8); 3·91 s, 3 H (OCH_3); 3·83 s, 3 H (OCH_3); 12·92 bs, 1 H (H-1); $J(1, 3) = 1·7$ Hz. ^{13}C NMR ($CDCl_3$): 128·0 (C-2); 98·3 (C-3); 150·5 (C-3a); 161·1 (C-4a); 112·5 (C-5); 125·1 (C-6); 122·7 (C-7); 118·7 (C-8); 117·6 (C-8a); 134·4 (C-1a); 169·2, 167·9 ($COOCH_3$); 144·8 (C-9); 110·7 (C-10); 52·4, 53·0 (OCH_3).

Dimethyl 1-*methylbenzo*[b]*furo*[3,2-b]-2-*pyrrolylbutenedioate* (VIII) was prepared analogously from 1-methylbenzo[*b*]furo[3,2-*b*]pyrrole (*IIb*). Yield 36%, m.p. 136°C (methanol). For $C_{17}H_{15}$·NO_5 (313·5) calculated: 65·17% C, 4·82% H, 4·47% N; found: 64·72% C, 4·84% H, 4·48% N. ^{1}H NMR ($CDCl_3$): 6·37 s, 1 H (H-3); 6·05 s, 1 H (H-10); 7·20–7·80 m, 4 H (H-5, H-6, H-7, H-8); 3·98 s, 3 H ($COOCH_3$), 3·97 s, 3 H ($COOCH_3$); 3·79 s, 3 H ($N—CH_3$). ^{13}C NMR ($CDCl_3$): 128·9 (C-2); 96·8 (C-3); 148·5 (C-3a); 160·1 (C-4a); 112·6 (C-5); 124·6 (C-6); 122·8 (C-7); 117·2 (C-8); 118·2 (C-8a); 130·3 (C-1a); 167·7, 165·7 ($COOCH_3$); 140·9 (C-9); 112·6 (C-10); 51·9, 53·0 (OCH_3); 35·28 ($N—CH_3$); ^3J(CO, H-10) = 10·6 Hz.

Dimethyl 3-Acetylaminodibenzofuran-1,2-dicarboxylate (*IX*)

A mixture of 1-acetylbenzo[*b*]furo[3,2-*b*]pyrrole (*IIc*; 3·98 g; 20 mmol), dimethyl butynedioate (3·55 g; 25 mmol) and acetonitrile (25 ml) was refluxed for 14 days. The white precipitate was collected; yield 4·00 g (59%), m.p. 243—245°C (methanol). For $C_{18}H_{15}NO_6$ (341·3) calculated: 63·34% C, 4·43% H, 4·10% N; found: 63·24% C, 4·45% H, 4·27% N. ^{1}H NMR ($CDCl_3$): 8·18 st, 1 H (H-4); 7·25—7·90 m, 4 H (H-arom); 3·99 s, 3 H ($COOCH_3$); 3·78 s, 3 H ($COOCH_3$); 10·1 bs, 1 H (NH). Mass spectrum, *m/z* (%): 341 (91), 309 (28), 299 (100, 294 (28), 267 (25), 237 (18), 209 (18), 18 (47), 43 (22), 29 (37·5).

Dimethyl 3-Aminodibenzofuran-1,2-dicarboxylate (*X*)

Dilute hydrochloric acid (10 ml; 1 : 1) was added to a solution of *IX* (3·41 g; 10 mmol) in a sufficient amount of methanol (about 700 ml) and the mixture was refluxed for 4 h, concentrated (to 50 ml) and poured into a solution of sodium hydrogen carbonate (5%; 50 ml). The precipitate was collected on a filter; yield 2·09 g (70%), m.p. 136—138°C (methanol). For $C_{16}H_{13}NO_5$ (299·3) calculated: 64·21% C, 4·38% H, 4·68% N; found: 64·30% C, 4·38% H, 4·68% N. ^{1}H NMR ($CDCl_3$): 7·02 s, 1 H (H-4), 7·25—7·80 m, 4 H (H-arom); 3·83 s, 3 H ($COOCH_3$); 4·00 s, 3 H ($COOCH_3$); 6·80 bs, 2 H (NH_2).

Dimethyl Benzofuran-1,2-dicarboxylate (*XI*)

A solution of *X* (2·99 g; 10 mmol) in dimethylformamide (14 ml) was added at 50°C to a vigorously stirred solution of pentyl nitrite (1·76 g; 15 mmol) in dimethylformamide (6 ml). After heating to 60°C for 5 h the mixture was cooled and poured into water. The precipitate was collected, washed with water and crystallized to give 1·42 g (50%) of *XI*, m.p. 121—123°C (methanol) (reported[10] m.p. 121—123°C). ^{1}H NMR ($CDCl_3$): 8·10 d, 1 H (H-3); 7·89 d, 1 H (H-4); 7·25 to 8·00 m, 4 H (H-arom); 3·90 s, 3 H ($COOCH_3$); 4·06 s, 3 H ($COOCH_3$); $J(3, 4) = 8·7$ Hz.

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Translated by M. Tichý.