PYRROLOINDOLES.

12.* SYNTHESIS OF 1H, 10H-BENZO[e]PYRROLO[3,2-g]INDOLE

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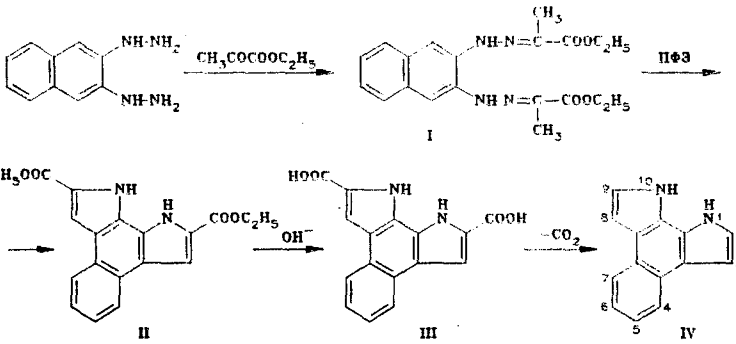
Cyclization of ethyl pyruvate 2,3-naphthylenehydrazone in polyphosphate ester gives 2,9-diethoxycarbonyl-1H,10H-benzo[e]pyrrolo[3,2-g]indole, which on hydrolysis and decarboxylation of the resulting acid affords the unsubtituted 1H,10H-benzo[e]pyrrolo[3,2-g]indole.

Substituted benzopyrroloindoles have been the subject of a few reports [2-4]. In order to examine the mutual effects of the benzene and pyrrole moieties in the benzindole molecule, we have synthesized the hitherto unknown benzopyrroloindole, unsubstituted in the α- and β-positions of the pyrrole rings.

1H,10H-Benzo[e]pyrrolo[3,2-g]indole (IV) was obtained from 2,3-naphthylenedihydrazine as follows [5].



Cyclization of ethyl pyruvate 2,3-naphthylenehydrazone (I) in polyphosphate ester (PPE), followed by hydrolysis of the resulting 2,9-diethoxycarbonyl-1H,10H-benzo[e]pyrrolo[3,2-g]indole (II) and decarboxylation of the diacid (III) gave the unsubstituted benzopyrroloindole (IV).

The structures of the benzopyrroloindoles (II-IV) were established by their IR, UV, PMR, and mass spectra. The IR spectra of (II-IV) contained characteristic absorption for pyrrole NH [6], and those of (II) and (III) for C=O. In the UV spectrum of the benzopyrroloindole

TABLE 1. PMR Spectra

Compound*	δ, ppm								J, Hz					
	1-H, 10-H	2-H, 9-H	3-H, 8-H	4-H, 7-H	5-H, 6-H	CH_2	CH_3	COOH	1,2	1,3	2,3	4,5	4,6	others
II	11,7, br.s.	—	7,72, br.s.	8,24, d.d.	7,36, d.d.	4,38, q	1,39, t	—	—	—	—	6,0	3,2	7,0 (CH_2CH_3)
III	11,6, br.s.	—	7,65, d	8,17, d.d.	7,41, d.d.	—	—	12,8, br.s.	—	2,0	—	5,8	3,3	—
IV	10,3, br.s.	7,17, d.d.	7,02, d.d.	8,18 d.d.	7,33, d.d.	—	—	—	2,6	2,4	3,0	6,3	3,2	—

*Compounds (II) and (III) in DMSO-D_6, and (IV) in acetone-D_6.

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*For communication 11, see [1].

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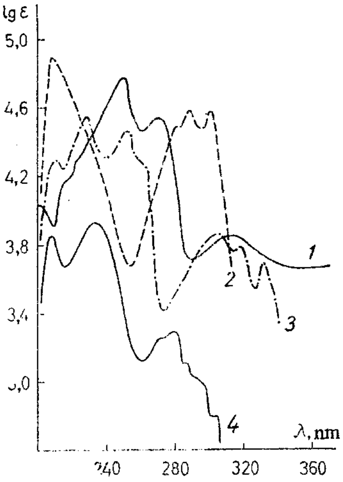

Fig. 1. UV spectra. 1) 1H,10H-benzo[e]pyrrolo[3,2-g]indole, 2) 3H,6H-pyrrolo[3,2-e]indole, 3) [4,5]benzindole, 4) 1H,6H-pyrrolo-[2,3-e]indole.

(IV), the absorption band is shifted bathochromically in comparison with the spectra of [4,5]benzindole and pyrroloindoles (Fig. 1) as a result of the formation of an extended π-conjugated system. The PMR spectra of the benzopyrroloindoles were in accordance with the symmetrical structures (II-IV) (see Table 1). In the PMR spectrum of the unsubstituted heterocycle (IV), the signal for the 3-H proton was shifted to lower field in comparison with the analogous signals for benz[6,7]indole [7] and angular pyrroloindoles [8, 9]. This shift in the signal for the pyrrole β-proton is due to strong steric interaction with the α-protons of the naphthalene ring, as is also seen in the PMR spectrum of benz[4,5]indole [7]. In the mass spectrum of the benzopyrroloindole(IV), the strongest peak is that for M^+, the subsequent fragmentation of which is in accordance with the proposed structure:

$$206^*\ (100)\xrightarrow{-\mathrm{H}}205\ (34)\xrightarrow{-\mathrm{HCN}}178\ (14)\xrightarrow{-\mathrm{HCN}}151\ (14);\ 206\ (100)\xrightarrow{-\mathrm{C_2H_5N}}103\ (25).$$

EXPERIMENTAL

The progress of the reactions and the purities of the compounds obtained were followed by TLC on Silufol UV-254. Preparative chromatography of (II-IV) was carried out on silica, particle size 100-250 μ. IR spectra were obtained on a UR-20 instrument in vaseline oil, UV spectra on a Specord spectrophotometer (in ethanol, $c = 10^{-5}$ mole/liter), PMR spectra of (II-IV) on a Varian CFT-20 spectrometer (internal standard TMS), and mass spectra on a NERMAG R-10-10 instrument (direct introduction into the ion source), ionizing electron energy 70 eV.

Ethyl Pyruvate 2,3-Naphthylenehydrazone (I). To a suspension of 4 g (21 mmole) of 2,3-naphthylenehydrazine [10] in 50 ml of ethanol was added a solution of 8 ml (73 mmole) of ethyl pyruvate in 5 ml of ethanol. After one hour, the product was filtered off and dried to give 7.04 g (87%) of yellow crystals, mp 123-125°C. Found: C 62.5; N 7.0; H 15.0%. $C_{20}H_{24}N_4O_4$. Calculated: C 62.5; H 6.3; N 14.6%.

2,9-Diethoxycarbonyl-1H,10H-benzo[e]pyrrolo[3,2-g]indole (II). A mixture of 6.7 g (19 mmole) of (I) and 67 g of PPE was heated for 20 min at 100°C with stirring. The mixture was then treated with water, and the solid which separated was filtered off, washed with water until neutral, and dried to give a qualitative yield of (II), which was purified by preparative column chromatography (benzene—acetone, 1:1), mp 315-316°C, R_f 0.44 (benzene—ether, 3:1). IR spectrum: 3410, 3390, 3380, 3290 (NH), 1715, 1670 cm^{-1} (C=O). UV spectrum, λ_{max} (lg ε): 228 (4.34), 236 (4.55), 246 (4.52), 265 (4.65), 277 (4.66) 2.89 (4.44), 338 (4.56), 351 nm (4.58). Found: C 68.1; H 5.4; N 7.76%; M^+ 350. Fragmentation sequence: $M^+\ 350\ (76)\xrightarrow{-\mathrm{C_2H_5OH}}304\ (100)\xrightarrow{-\mathrm{C_2H_6OH}}258\ (30)\xrightarrow{-\mathrm{CO}}230\ (15)\xrightarrow{-\mathrm{HCN}}203\ (15)\xrightarrow{-\mathrm{HCN}}176\ (30);\ 304\ (100)\xrightarrow{\mathrm{CO}}276\ (23).$

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*Here and subsequently, the intensities of the m/z values relative to the main peak in the spectrum are given in brackets.

$C_{20}H_{18}N_2O_4$. Calculated: C 68.6; H 5.1; N 8.0%.

2.9-Dicarbonyl-1H,10H-benzo[e]pyrrolo[3,2-g]indole (III). To a suspension of 2.7 g (8 mmole) of (II) in 8 ml of propan-2-ol was added a solution of 11 g (190 mmole) of KOH in 40 ml of water, and the mixture boiled until solution was complete. The filtrate was acidified with HCl, and diluted to pH 1. The solid which separated was filtered off, washed with water until neutral, and dried to give 1.9 g (84%) of the benzopyrroloindole (III), mp 231-232°C, Rf 0.46 (benzene—acetone, 1:1). IR spectrum: 3250, 3380 (N—H), 1700, 1640 cm^{-1} (C═O). UV spectrum, λ_{max} (lg ε): 228 (4.24), 235 (4.33), 248 (4.32), 265 (4.45), 276 (4.47), 333 (4.31), 348 nm (4.33). Found: C 65.9; H 5.2; N 10.4%. $C_{16}H_{10}N_2O_4$. Calculated: C 65.3; H 3.4; N 9.5%.

1H,10H-Benzo[e]pyrrolo[3,2-g]indole (IV). In a flask fitted with a gas delivery tube was placed 3.3 g (11 mmole) of (III), and heated at 220°C for 8-10 min until evolution of CO_2 ceased. The product was cooled and extracted with acetonitrile. The extract was evaporated, and the residue purified by preparative column chromatography (benzene) to give 0.51 g (22%) of (IV), mp 180-181°C, Rf 0.36 (benzene—ether, 1:3). IR spectrum: 3450, 3400 cm^{-1} (NH), UV spectrum, λ_{max} (lg ε): 213 (4.17), 224 (0.43), 246 (4.79), 269 (4.54), 314 nm (3.86). Found: C 81.7; H 4.7; N 13.5%; M^+ 206. $C_{14}H_{10}N_2$. Calculated: C 81.6; H 4.9; N 13.6%. On treatment with Ehrlich's reagent at room temperature, a blue coloration was obtained.

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