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PYRROLOCARBAZOLES 2.*

SOME DERIVATIVES OF 3H-PYRROLO[2,3-c]CARBAZOLE

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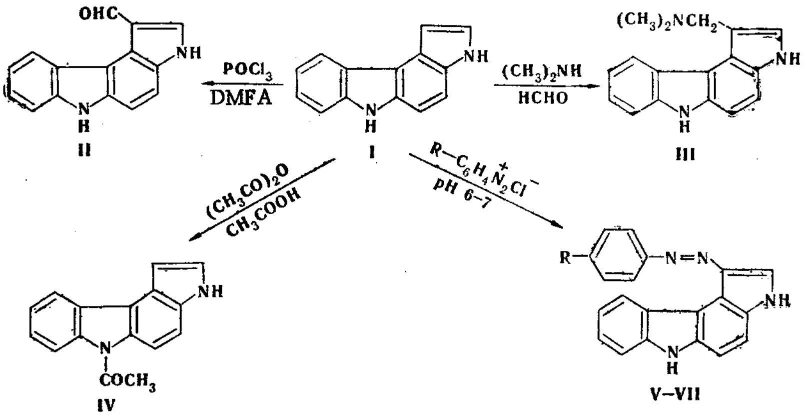
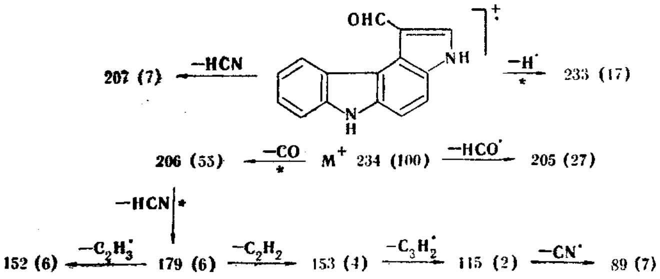
In the previous communication we described the synthesis of 3H-pyrrolo[2,3-c]carbazole [1]. In the present work, in order to investigate its reactivity, we studied certain electrophilic substitution reactions typical of the indole series (the Vilsmeier, Mannich, azo coupling, and acylation reactions).



V R=H; VI R=Cl; VII R=NO$_2$

In view of a certain structural similarity between pyrrolocarbazole and indole, the above-mentioned reactions were carried out with certain modifications under the conditions described for indole itself [2-5].



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*For Communication 1, see [1].

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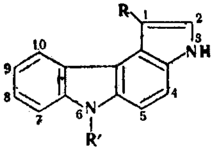
TABLE 1. Chemical Shifts (δ, ppm) and Spin–Spin Coupling Constants (J, Hz) in the PMR Spectra of Compounds (II–IV)

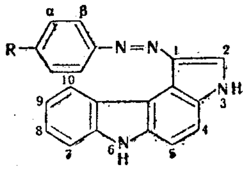


Compound	R	R′	δ, ppm													J, Hz	Solvent
			1-H	2-H	3-H	4-H	5-H	6-H	7-H	8-H	9-H	10-H	CHO	$-CH_3$	$-CH_2$		
II	CHO	H	—	8,31 d	10,59 bs	7,63* d	7,50* d	11,51 bs	7,1—7,5			9,33 q	10,02 s			$J_{2,3}=1,7$; $J_{4,5}=8,6$; $J_{9,10}=7,0$; $J_{8,10}=2,1$	Acetone-d_6
III	$(CH_3)_2NCH_2$	H	—	7,14 d	10,41 bs	7,33* d	7,25* d	10,59 bs	7,1—7,4			8,61 q	—	2,23 t	3,81 q	$J_{4,5}=8,7$; $J_{9,10}=7,4$; $J_{8,10}=1,6$	Acetone-d_6
IV	H	$COCH_3$	7,11 q	—†	10,60 bs	7,60* d	8,16* d	—	7,4—8,3				—	2,94 s	—	$J_{1,2}=J_{1,3}=2,5$; $J_{4,5}=8,8$	Acetone-d_6—$CDCl_3$ (1 : 1)

*Or vice versa.

†The signal overlaps the signal of the group of protons 7, 8, 9, and 10.

TABLE 2. Chemical Shifts (δ, ppm) and Spin–Spin Coupling Constants (J, Hz) of Azo Derivatives of 3H-Pyrrolo[2,3-c]carbazole



Compound	R	δ, ppm											J, Hz	Solvent
		2-H	3-H	4-H	5-H	6-H	7-H	8-H	9-H	10-H	α-H	β-H		
V	H	7,98 d	10,48 bs	7,61* d	7,46* d	11,29 bs	7,3—7,7			9,30 m	—†	8,04 d	$J_{3,2}=1,3$; $J_{4,5}=8,6$; $J_{9,10}=7,2$; $J_{\alpha,\beta}=8,5$; $J_{\beta,R}=1,8$	Acetone-d_6
VI	Cl	8,00 d	10,54 bs	7,63* d	7,48* d	11,37 bs	7,3—7,6			9,23 m	7,64 d	8,01 d	$J_{3,2}=1,6$; $J_{4,5}=8,7$; $J_{9,10}=7,2$; $J_{\alpha,\beta}=8,7$	The same
VII	O_2	8,09 d	10,59 bs	7,65* d	7,49* d	11,63 bs	7,3—7,5			9,16 m	8,50 d	8,50 d	$J_{3,2}=1,8$; $J_{4,5}=8,7$; $J_{9,10}=7,6$; $J_{\alpha,\beta}=9,1$	„ „

*Or vice versa.

†The signal lies in the region of the signal for the group of protons 7, 8, and 9.

By the formylation of compound (I) we obtained 1-formyl-3H-pyrrolo[2,3-c]carbazole (II), the structure of which was proved by its IR, UV, PMR, and mass spectra. In the PMR spectrum there is a considerable downfield shift of the signal for the 3-H and 10-H protons (Table 1) compared with the unsubstituted ring (9.96 and 8.19 ppm respectively) [1], and this is clearly due to the presence of the aldehyde group in the molecule. In the mass spectrum of compound (II) there is a strong peak for the molecular ion (M^+) with m/e 234, and the character of subsequent fragmentation and certain decomposition processes confirmed by the metastable transitions do not contradict the proposed structure.*

We established that compound (I) reacts fairly readily with dimethylamine in the Mannich reaction to form 1-dimethylamino-3H-pyrrolo[2,3-c]carbazole (III) with a quantitative yield.

The azo coupling reaction was realized in a 1:1 mixture of dioxane and water in neutral media with the diazonium salts obtained from aniline, p-chloroaniline, and p-nitroaniline.

The UV spectra, recorded in ethanol, demonstrated the similarity in the structures of compounds (V-VII). Absorption maxima are observed in the region of 402-406, 416-426, and 510-520 nm respectively. As expected, for the azo compounds (V) and (VI) the difference in the positions of the long-wave band is small (∿ 15 nm), and for the azo coupling product (VII) the maximum is shifted by 110 nm.

The PMR data for the azo compounds (V-VII) confirm their structure (Table 2). The shifts of all the assigned protons vary in line with the variation in the electronic characteristics of the substituents R, characterized by the Hammett σ_p constants, except for the shift of the 10-H proton. The latter varies inversely with variation of σ_p on account, clearly, of the influence of the substituent R on the 10-H atom, which has not so much electronic as steric character. Increase in the accepting characteristics of the substituent R assists conjugation between the unshared pairs of the nitrogen atoms and the benzene ring and leads to a reduction of the dipole–dipole interaction between the 10-H atoms and the hetero atoms. Here the electron density distribution in the whole molecule and, consequently, the ring current in the phenyl group also change.

In the PMR spectra of all the above-mentioned compounds the absence of a signal for the 1-H proton (7.00 ppm) indicates that the hydrogen at position 1 of the pyrrolocarbazole ring is substituted.

During acylation of compound (I) with acetic anhydride under the conditions described for indole we isolated a product corresponding to the structure of 6-acetyl-3H-pyrrolo[2,3-c]carbazole (IV). The presence of the acetyl group at position 6 of the pyrrolocarbazole ring is demonstrated by the absence of a signal for the 6-H proton of the NH group and by the observed quartet for the 1-H proton (spin–spin coupling with the 2-H and 3-H protons). Resinification of the product occurs during acylation under drastic conditions.

Thus, the reactions of pyrrolocarbazole (I) with weak electrophiles occur at the most reactive β position, and the nitrogen atom of the carbazole part of the molecule undergoes acetylation.

EXPERIMENTAL

The IR spectra were recorded in suspensions in Vaseline oil on a UR-20 spectrophotometer. The UV spectra were recorded in ethanol on a Specord UV-instrument. The PMR spectra were recorded on a CFT-20-16K spectrometer with TMS as internal standard. The mass spectra were recorded on an MX-1303 instrument with direct injection of the substance into the ion source under the following conditions: Ionization potential 50 eV, accelerating potential 2 kV, cathode emission current 1.5 mA.

1-Formyl-3H-pyrrolo[2,3-c]carbazole (II). To 0.83 ml (0.009 mole) of freshly distilled dimethylformamide at 0°C we slowly added 0.24 ml of phosphorus oxychloride. The reaction mass was kept at room temperature for 1 h, and 0.5 g (0.002 mole) of compound (I), dissolved in 2 ml of DMFA, was added. The mixture was heated to 40°C for 3 h. It was then cooled, 6 g of crushed ice was added, and the mixture was made alkaline with 0.1 N sodium hydroxide solution. The precipitate was filtered off, washed with water, and dried. The product was

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*Here and subsequently the m/e values are given, and the relative intensities of the ion peaks as percentages of the maximum are given in parentheses.

purified on a column of silica gel 100/250 μ with a 2:1 mixture of ethyl acetate and petroleum ether as eluent. The yield of the pure reaction product was 0.4 g (71%); mp 244-245°C. IR spectrum: 3320, 3230 (NH), 1640 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 218 (4.76), 256 (4.32), 267 (4.26), 298 nm (4.43). Found, %: C 76.4; H 4.31; N 11.1. $C_{15}H_{10}N_2O$. Calculated, %: C 76.8; H 4.3; N 11.1.

1-(Dimethylaminomethyl)-3H-pyrrolo[2,3-c]carbazole (III). To 1.9 ml (0.002 mole) of a 33% aqueous solution of dimethylamine, while cooling, we slowly added 1.9 ml of glacial acetic acid and then 1 ml of 40% formalin and 0.5 g (0.002 mole) of compound (I). The mixture was kept at room temperature for 1 h, added to water, and made alkaline with 10% sodium hydroxide solution. The white precipitate was filtered off, washed with water, and dried over potassium hydroxide in a vacuum desiccator. The yield was 0.55 g (91%); mp 87-88°C. UV spectrum, λ_{max} (log ε): 210 (4.47), 223 (4.64), 244 (4.56), 317 (4.37), 333 nm (4.25). Found, %: N 16.1. $C_{17}H_{17}N_3$. Calculated, %: N 15.9. Methyl sulfate derivative of (III), mp 189-190°C. Found, %: N 11.1; S 7.9. $C_{19}H_{23}N_3O_4S$. Calculated, %: N 10.7; S 8.2.

6-Acetyl-3H-pyrrolo[2,3-c]carbazole (IV). A mixture of 0.2 g (0.001 mole) of compound (I), 0.9 ml (0.001 mole) of acetic anhydride, and 0.07 ml (0.001 mole) of acetic acid was boiled for 5 h. The mixture was cooled and added to water, and the precipitate was filtered off and dried. The product was purified on a column of silica gel 100/250 μ with 1:1 mixture of ether and petroleum ether as eluent. The yield was 0.18 g (75%); mp 179-180°C. IR spectrum: 3270 (NH), 1670 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 223 (4.55), 250 (4.37), 320 (4.29), 332 nm (4.26). Found, %: C 77.3; H 5.2; N 11.2. $C_{16}H_{12}N_2O$. Calculated, %: C 77.4; H 4.8; N 11.3.

1-Phenylazo-3H-pyrrolo[2,3-c]carbazole (V). To a solution of 0.2 g (0.001 mole) of compound (I) in 10 ml of dioxane and 10 ml of water in the presence of 1 g of sodium acetate at 0°C we added a solution of 0.001 mole of benzenediazonium chloride, obtained by the usual method. The azo coupling reaction was realized at pH 6-7 for 3 h, and the compound was extracted with ether. The product was chromatographed on a column of silica gel with a 1:1 mixture of ether and hexane as eluent. The yield was 0.22 g (66%); mp 205-206°C. IR spectrum: 3340, 3420 (NH), 1460 cm^{-1} (—N=N—). UV spectrum, λ_{max} (log ε): 206 (4.65), 317 (4.24), 412 nm (4.06). Found, %: C 77.4; H 4.6; N 17.8. $C_{20}H_{14}N_4$. Calculated, %: C 77.4; H 4.5; N 18.0.

1-(4'-Chlorophenylazo)-3H-pyrrol [2,3-c]carbazole (VI). Compound (VI) was obtained by the method described above from 0.2 g (0.001 mole) of compound (I) and an equimolar amount of p-chlorobenzenediazonium chloride. The yield was 0.23 g (76%); mp 242-243°C. IR spectrum: 3425, 3390 (NH), 1410 (—N=N—), 720 cm^{-1} (C—Cl). UV spectrum, λ_{max} (log ε): 204 (4.51), 227 (4.73), 326 (4.40), 422 nm (4.24). Found, %: C 69.5; H 3.7; Cl 10.5; N 16.6. $C_{20}H_{13}ClN_4$. Calculated %: C 69.6; H 3.7; Cl 10.3; N 16.2.

1-(4'-Nitrophenylazo)-3H-pyrrolo[2,3-c]carbazole (VII). Compound (VII) was obtained by the method described for compound (V) from 0.2 g (0.001 mole) of compound (I) and an equimolar amount of p-nitrobenzenediazonium chloride. The yield was 0.3 g (88%); mp 274-275°C. IR spectrum: 3415, 3380 (NH), 1420 cm^{-1} (—N=N—). UV spectrum, λ_{max} (log ε): 205 (4.31), 223 (4.58), 322 (4.38), 522 nm (4.12). Found, %: N 19.3. $C_{20}H_{13}N_5O_2$. Calculated, %: N 19.7.

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