BISINDOLES.

4.* ELECTROPHILIC SUBSTITUTION IN THE 1H, 6H-INDOLO[7,6-g]INDOLE SERIES

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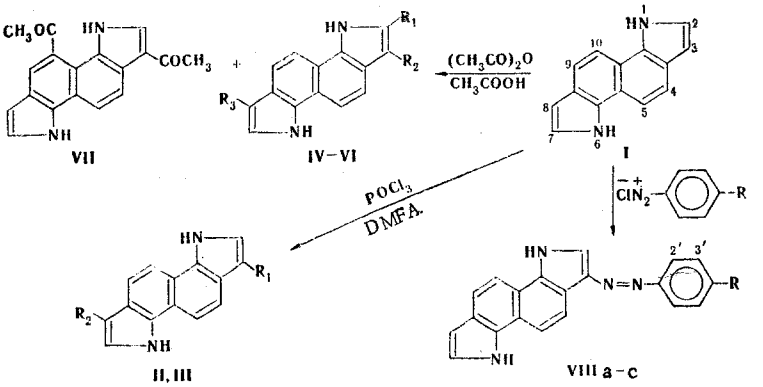
We have previously synthesized the progenitor of a new heterocyclic system 1H, 6H-indolo[7,6-g]indole (I) [2, 3]. In this communication we shall present the results of an investigation of the ability of this compound to undergo electrophilic substitution reactions in the example cases of acylation and nitrogen-coupling reactions.



II R_1=CHO, R_2=H; III R_1=R_2=CHO; IV R_1=H, R_2=$COCH_3$, R_3=H; V R_1=$COCH_3$, R_2=H, R_3=H; VI R_1=$COCH_3$, R_2=H, R_3=$COCH_3$; VIII a R=H; b R=Cl; c R=NO_2

Under the conditions described for the synthesis of indole-3-aldehyde [4] by Vilsmeier fomylation, we observed the formation of a mixture of 3-formyl-1H, 6H-indolo[7, 6-g]indole (II) and 3,8-diformyl-1H, 6H-indolo[7, 6-g]indole (III) in equal proportions. When a threefold excess of Vilsmeier's complex was used, dialdehyde III was obtained with a quantitative yield. 1H, 6H-Indolo[7, 6-g]indole did not react with N,N-dimethylacetamide at 70-100°C, further increase in the temperature caused resinification, and there were no acetylation products in the reaction mixture. Similar results were obtained in the case of the acetylation of angular benzindoles under the conditions of the Vilsmeier reaction. This is apparently due to the reduced electrophilic properties of the complex with N,N-dimethylacetamide, as well as the lowering of the electron density in position 3 of the indole ring in the case of condensed systems [5, 6].

The acetylation of 1H, 6H-indolo[7, 6-g]indole by acetic anhydride in glacial acetic acid proceeded with low yields and produced a mixture of acetylated products. They were separated by column chromatography. The following were isolated: 3-acetyl-1H, 6H-indolo[7, 6-g]indole (IV), 2-acetyl-1H, 6H-indolo[7, 6-g]indole (V), 2,8-diacetyl-1H, 6H-indolo[7, 6-g]indole (VI), and 3,10-diacetyl-1H, 6H-indolo[7, 6-g]indole (VII). The yield of the monoacetyl derivatives significantly exceeded the yields of the diacetyl derivatives owing to the deactivation of the aromatic ring by the electron-acceptor substituent [7-10]. The occurrence of acetylation in the benzene part of the molecule is apparently attributable to the additional activation of the reactive α-naphthalene position due to the influence of the pyrrole rings. The orientation we observed, which is somewhat unusual for indoles, in the case of the acetylation by acetic anhydride is also displayed in the case of dibenzindole

*For report 3 see [1].

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TABLE 1. Parameters of the PMR Spectra of I–VII in Acetone-d_6

Compound	Chemical shifts, δ, ppm												Spin–spin coupling constants, J, Hz
	1H	2H	3H	4H	5H	6H	7H	8H	9H	10H	CHO	CH_3	
I	10,9 bs	7,31 dd	6,61 dd	7,70 dd	7,96 d	10,9 bs	7,31 dd	6,61 dd	7,70 dd	7,96 d	—	—	$J_{1,2}=J_{6,7}=2,6$; $J_{1,3}=J_{6,8}=2,1$; $J_{1,4}=J_{6,9}=0,5$; $J_{2,3}=J_{7,8}=3,2$; $J_{4,5}=J_{9,10}=8,6$
II	12,0 bs	8,19 d	—	8,18 dd	8,37 d	11,3 bs	7,41 dd	6,67 dd	8,02 dd	7,80 d	10,12 s	—	$J_{1,2}=3,1$; $J_{1,4}=0,8$; $J_{4,5}=8,6$; $J_{6,7}=2,6$; $J_{6,8}=2,0$; $J_{6,9}=0,8$; $J_{7,8}=3,0$; $J_{9,10}=8,9$
III[a]	11,9 bs	8,19 d	—	8,42 dd	8,20 d	11,9 bs	8,19 d	—	8,42 dd	8,20 d	10,14 s	—	$J_{1,2}=J_{6,7}=3,1$; $J_{1,4}=J_{6,9}\approx 0,7$; $J_{4,5}=J_{9,10}=8,8$
IV[a]	11,5 bs	8,14 d	—	8,11 dd	8,46 d	11,0 bs	7,35 dd	6,63 dd	7,98 dd	7,75 d	—	2,51 s	$J_{1,2}=3,2$; $J_{1,4}=0,7$; $J_{4,5}=8,6$; $J_{6,7}=2,6$; $J_{6,8}=2,0$; $J_{6,9}=0,6$; $J_{7,8}=3,0$; $J_{9,10}=8,6$
V	11,4 bs	—	7,43 d	8,34 dd	7,78 d	11,2 bs	7,41 dd	6,66 dd	8,06 dd	7,75 d	—	2,55 s	$J_{1,3}=1,9$; $J_{1,4}=0,7$; $J_{4,5}=8,7$; $J_{6,7}=2,7$; $J_{6,8}=2,0$; $J_{6,9}=0,7$; $J_{7,8}=3,0$; $J_{9,10}=8,8$
VI[b]	12,4 bs	—	7,63 d	8,26 dd	7,96 d	12,7 bs	8,19 d	—	8,62 dd	8,50 d	—	2,56 s (at C_2) ~2,5 (at C_8) 2,56 s (at C_2) 2,95 s (at C_{10})	$J_{1,3}=1,9$; $J_{1,4}=0,9$; $J_{4,5}=8,7$; $J_{6,7}=3,0$; $J_{6,9}=0,9$; $J_{9,10}=8,7$
VIIIc	12,4 bs	8,19 d	—	8,66 dd	8,20 d	11,5 bs	7,48 dd	6,79 dd	8,78 d	—	—		$J_{1,2}=3,2$; $J_{1,4}\approx 0,7$; $J_{4,5}=8,7$; $J_{6,7}=2,6$; $J_{6,8}=2,0$; $J_{6,9}\approx 0,7$; $J_{7,8}=3,2$

[a]At 50°C. [b]In DMSO-d_6 at 50°C.

TABLE 2. Parameters of the PMR Spectra of VIIIa–VIIIc in Acetone-d_6 at 50°C

Compound	Chemical shifts, δ, ppm											Spin–spin coupling constants, J, Hz
	1H	2H	4H	5H	6H	7H	8H	9H	10H	aromatic		
VIIIa	11,3 bs	7,82 d	8,20 dd	7,77 dd	11,1 bs	7,40 dd	6,65 dd	8,05 dd	7,76 d	7,3–7,9		$J_{1,2}=2,0$; $J_{1,4}=0,7$; $J_{4,5}=8,7$; $J_{6,7}=2,5$; $J_{6,8}=2,0$; $J_{6,9}=0,5$; $J_{7,8}=3,2$; $J_{9,10}=8,8$
										2′	3′	
VIIIb	11,4 bs	7,82 bs	8,19 dd	7,78 d	11,1 bs	7,42 dd	6,64 dd	8,04 dd	7,77 d	7,88 d	7,55 d	$J_{1,2}\approx 2$; $J_{1,4}=0,9$; $J_{4,5}=8,7$; $J_{6,7}=2,6$; $J_{6,8}=2,0$; $J_{6,9}=0,7$; $J_{7,8}=3,0$; $J_{9,10}=8,8$; $J_{2',3'}=8,8$
VIIIc	11,6 bs	7,57 bs	8,22 dd	7,78 d	11,1 bs	7,43 dd	6,64 dd	8,06 dd	7,78 d	8,03 d	8,40 d	$J_{1,2}\approx 2$; $J_{1,4}=0,6$, $J_{4,5}=8,6$; $J_{6,7}=2,3$; $J_{6,8}=2,0$; $J_{6,9}=0,5$; $J_{7,8}=3,1$; $J_{9,10}=8,6$; $J_{2',3'}=9,1$

[11]. The absence of the formation of the 2-formyl derivative in the case of the reaction with Vilsmeier's complex is apparently due to the great selectivity of this weak electrophile.

The nitrogen coupling of 1H, 6H-indolo[7,6-g]indole (I) with various diazo compounds with an ambient pH equal to 6-8 and a molar ratio between the substrate and the diazonium salts equal to 1:3 resulted in the formation mainly of the corresponding 3-phenylazo derivatives: 3-phenylazo-1H, 6H-indolo[7,6-g]indole (VIIIa), 3-(4'-chlorophenylazo)-1H, 6H-indolo[7,6-g]indole (VIIIb), and 3-(4'-nitrophenylazo)-1H, 6H-indolo[7, 6-g]indole (VIIIc). In contrast to the acylation reaction, the formation of mainly monosubstituted derivatives in the case of the nitrogen-coupling reaction is apparently due to the weak electrophilicity of the ArN_2^+ ion, which is insufficient for an interaction with the aromatic system, whose electron density has already been reduced by the introduction of a phenylazo group. The decrease in the electron density in positions 8 and 7 of compounds VIIIa-VIIIc is indicated by the downfield displacement of the signals of the protons in these positions in the PMR spectra relative to the signals of the corresponding protons in unsubstituted indoloindole I (Tables 1 and 2).

The structure of all the compounds synthesized was proved by investigating their PMR spectra and confirmed by the data from elemental analysis, IR spectroscopy, UV spectroscopy, and mass spectrometry.

According to Tables 1 and 2, the introduction of electron-acceptor groups results in deshielding of the protons in comparison to unsubstituted indoloindole I. Alteration of the position of the substituent (2 or 3) scarcely alters the overall effect of the change in the electron density in the molecule, but it does result in considerable redistribution of the electron density (compare the shifts of 4H and 5H of compounds IV and V in Table 1). The introduction of another substituent into the molecule causes a smaller overall change in charge.

The complete assignment of the lines in the PMR spectra of compounds I-VIII (Tables 1 and 2) proved to be possible owing to the existence of the long-range spin–spin interaction constants $J_{NH, CH}$ of the transoid type through five bonds [12] and the difference extents of deuteration of the NH protons due to exchange with the D_2O found in acetone-d_6. The rate of the D exchange is higher, the greater is the acidity of the protons indicated, which depends on the nature and position of the electron-acceptor substituents. The latter also mainly determines the downfield shift of the signal of the nearest NH group. The deuteration process causes changes in the multiplicity of the signals of the protons interacting with NH: Singlets ($J_{ND, CH} \approx 0$) appear on a background of doublets ($J_{NH, CH}$ = 0.5 to 3 Hz). Thus, the spectra of some compounds, which require prolonged accumulation (~ 30 min) because of their limited solubility, show smoothed "triplets" or broadened singlets (Table 2, compounds VIIIb and VIIIc, 2H).

Compound VII does not show a great tendency to undergo deuteration, as might have been expected on the basis of the shift of the 1H proton. This is due to the participation of the latter in an intramolecular hydrogen bond with the carbonyl group $COCH_3$ in position 10. The latter, as follows from a comparison of the shifts of the protons in positions 4, 5, 9, and 10 for 3-formylindoloindole II and 3-acetylindoloindole IV (Table 1), is the most shielded and consequently the most reactive of all the positions in the benzene rings (although, as we know, a PMR-chemical-shift–electron-density correlation is not observed in the general case).

In the IR spectra of compounds II-VIII the characteristic absorption bands of the NH groups are observed in the 3200-3400-cm^{-1} region, the absorption of the aldehyde C=O group in compounds II and III is manifested in the form of broad intense bands in the 1640-1660 cm^{-1} region, and the carbonyl groups in compounds IV-VII are manifested in the form of a band of low intensity in the 1720-1750-cm^{-1} region and an intense band at 1620-1660 cm^{-1}. The absorption bands caused by the stretching vibrations of the azo groups have low intensities in compounds VIIIa-VIIIc and appear in the 1400-1429-cm^{-1} region, as in the case of the corresponding azo compounds of indole [13].

The UV spectrum of compound II, as expected, is less structured than is the spectrum of unsaturated heterocycle I (Fig. 1). The introduction of a second formyl group (compound III) results in even greater smoothing of the vibrational structure and a bathochromic shift of the absorption bands (Fig. 1). In the spectra of compounds VIIIa-VIIIc the position of the shortwave maximum remains unchanged in comparison to the spectrum of the unsubstituted indoloindole: The maxima in the 280-360-nm region also vanish in the case of compounds VIIIb and VIIIc, and an additional absorption band appears at 400-560 nm.

EXPERIMENTAL

The course of the reaction and the purity of the compounds were monitored in Silufol UV-254. The preparative chromatography of compounds II-VIIIa was carried out on SiO_2 with particle dimensions equal to 100 to 250 μ, and that of compounds VIIIb and VIIIc was carried out on Al_2O_3 (second activity grade). The IR spectra

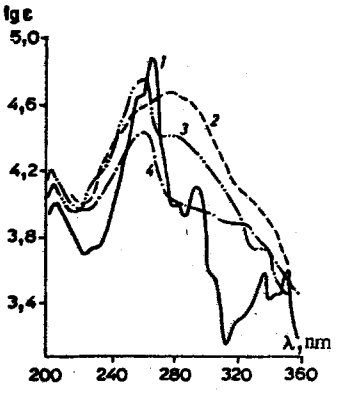


Fig. 1. Electronic spectra: 1) I; 2) III; 3) II; 4) VIIIa.

were recorded on a UR-20 instrument in liquid petrolatum, and the UV spectra were recorded on a Specord spectrophotometer in ethanol. The PMR spectra of compounds I-VIII were recorded on a Varian CFT-20 spectrometer, and the internal reference was TMS. The accuracy of the measurement of the chemical shifts was ±0.02 ppm, and that of the spin–spin coupling constants was ±0.1 Hz. The mass spectra were recorded on an MKh-1303 instrument with a modified system for introducing the sample (direct introduction into the ion source) and an energy of the ionizing electrons equal to 50 eV.

3-Formyl-1H, 6H-indolo[7, 6-g]indole (II). A 0.4-ml portion (4 mmole) of freshly distilled $POCl_3$ was added dropwise at 10–15°C to 1.4 ml (17 mmole) of distilled DMFA. The resulting mixture was given a dropwise addition of a solution of 0.5 g (2 mmole) of compound I in 5 ml of DMFA at 20–30°C. The mixture was stirred for 1 h at 38–40°C. A yellow precipitate formed. The reaction mass was poured into ice, a solution of 0.76 g of NaOH in 4 ml of water was added to pH 6–7, and then 20 ml of water were added, and the mixture was boiled for 3–5 min. The precipitate was filtered, washed to a neutral reaction, and dried. The yield was 0.58 g (92%).

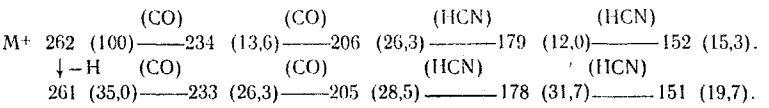
The chromatogram (the eluent was ethyl acetate) showed two spots with R_f 0.71 (II) and 0.38 (III). The separation of this mixture into individual compounds was carried out in a column. Compound II was eluted by a 2:1 benzene–ether mixture. The yield was 15 mg (2.4% relative to the original I). Compound III was eluted by ethyl acetate. The yield was 15 mg (2.3% relative to the original I). Aldehyde II was recovered in the form of colorless crystals with mp 282–283°C. IR spectrum: 3420, 3260 (NH), 1640 (C=O), shoulder at 1655 cm^{-1}. UV spectrum, λ_{max} (log ε): 204 (4.16), 233 (4.23), 252 (4.60), 261 (4.78), 282 (4.44), 338 (3.75), 354 nm (3.62). Found: C, 71.4; H, 4.4; N, 11.1%; M 234. The dissociation scheme is as follows (m/e and relative intensity):

$$M^+\ 234\ (100) \xrightarrow[m^*\ 232]{-H} 233\ (27{,}8) \xrightarrow{(CO)} 205\ (25{,}8) \xrightarrow{(HCN)} 178\ (26{,}3) \xrightarrow{(HCN)} 151\ (5{,}3).$$

$$\xrightarrow[m^*\ 181{,}4]{(CO)} 206\ (22{,}0) \xrightarrow{(HCN)} 179\ (4{,}7) \xrightarrow{(HCN)} 152\ (2{,}4).$$

Calculated for $C_{15}H_{10}N_2O \cdot H_2O$: C, 71.4; H, 4.8; N, 11.1%; M 252. The compound produced a pink color with Ehrlich's reagent at room temperature.

3,8-Diformyl-1H, 6H-indolo[7,6-g]indole (III). A 3.72-ml portion (0.048 mole) of redistilled DMFA was cooled to −5°C, and 1.08 ml (0.012 mole) of freshly distilled $POCl_3$ were added dropwise. The mixture was stirred at room temperature for 40 min. The mixture was cooled again to −5°C and slowly given an addition of a solution of 0.82 g (4 mmole) of compound I in 10 ml of DMFA at a temperature no greater than 0°C. The mixture was stirred at 40°C for 2 h. A yellow precipitate formed. The latter was given an addition of 13 ml of ice water, then transferred to ice (~2 g) with the use of an additional 20 ml of water, and given a dropwise addition of solution of 3.4 g of NaOH in 9 ml of water. The precipitate was filtered, washed with cold water to a neutral reaction, and dried. The yield was 0.99 g (95%). The product was recrystallized from ethanol with charcoal, the decomposition temperature was 340°C, and R_f was 0.38 (ethyl acetate). IR spectrum: 3230 (NH), 1660 (C=O), shoulder at 1610 cm^{-1}. UV spectrum, λ_{max} (log ε): 208 (4.14), 252 (4.58); 260 (4.61), 276 (4.71), 287 (4.66), 320 (4.19), 335 (4.04), 350 nm (3.82). Found: C, 73.5, H, 4.3; N, 10.6%; M 262. The dissociation scheme is as follows (m/e and relative intensity):



Calculated for $C_{16}H_{10}N_2O_2$: C, 73.3; H, 3.8; N, 10.7%; M 262.

Acetylation of 1H, 6H-Indolo[7, 6-g]indole. A 0.41-g portion (2 mmole) of I was given an addition of 10 ml of redistilled acetic anhydride and 14.7 ml of glacial acetic acid. The mixture was boiled for 17 h and evaporated in a vacuum. This yielded 0.64 g. The chromatogram of this residue (1:1 benzene–acetone) showed several spots. The separation of this mixture into individual compounds was carried out in a column.

3-Acetyl-1H, 6H-indolo[7, 6-g]indole (IV). This compound was eluted by a 1:1 benzene–ether mixture. The yield was 15 mg (~4% relative to the original I). It presented itself as yellow crystals with a decomposition temperature of 177°C and R_f 0.39 (2:1 benzene–acetone). IR spectrum: 3430, 3300, 3220-3240 (NH), 1730, shoulder at 1720, 1650 (C=O), shoulder at 1620 cm^{-1}. Found: C, 77.0; H, 5.6; N, 10.9%; M 248. Calculated for $C_{16}H_{12}N_2O$: C, 77.4; H, 4.8; N, 11.3%; M 248. The compound produced a pink color with Ehrlich's reagent at room temperature.

2-Acetyl-1H, 6H-indolo[7, 6-g]indole (V). This compound was eluted by a 10:3 benzene–ether mixture. The yield was 20 mg (4% relative to the original I). It presented itself as yellowish crystals with a decomposition temperature of 259°C and Rf 0.49 (10:3 benzene–acetone). IR spectrum: 3420, 3310 (NH), 1660, 1725 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 204 (4.10), 249 (4.51), 255 (4.59), 276 (4.24), 287 (4.40), 360 nm (4.26). Found: C, 77.5; H, 5.3; N, 11.2%; M 248. Calculated for $C_{16}H_{12}N_2O$: C, 77.4, H, 4.8; N, 11.3%; M 248. The compound produced a pink color with Ehrlich's reagent at room temperature.

2,8-Diacetyl-1H, 6H-indolo[7, 6-g]indole (VI). This compound was eluted by ether. The yield was 10 mg (1.8% relative to the original I). The decomposition temperature was 190°C, and the Rf value was 0.33 (2:1 benzene–acetone). IR spectrum: 3325, 3290, 3200 (NH), 1645, 1730-1750 cm^{-1} (C=O). Found: C, 73.9; H, 5.0; N, 9.6%; M 290. Calculated for $C_{18}H_{14}N_2O_2$: C, 74.5, H, 4.8; N, 9.7%; M 290. The compound produced a yellow color with Ehrlich's reagent at room temperature. It presented itself as a yellowish brown powder.

3,10-Diacetyl-1H, 6H-indolo[7, 6-g]indole (VII). This compound was eluted by a 2:1 benzene ether mixture. The yield was 10 mg (1.8%). It presented itself as yellow crystals, with a decomposition temperature of 204°C and R_f 0.36 (10:3 benzene–acetone). IR spectrum: 3300, shoulder at 3340, 3120-3130 (NH), 1725, 1630-1650 cm^{-1} (C=O). Found: C, 74.4; H, 5.4; N, 9.3%; M 290. Calculated for $C_{18}H_{14}N_2O_2$: C, 74.5; H, 4.8; N, 9.7%: M 290. The compound produced a violet color with Ehrlich's reagent at room temperature after standing.

3-Phenylazo-1H, 6H-indolo[7, 6-g]indole (VIIIa). A solution of 0.41 g (2 mmole) of I in 72 ml of dioxane and 20 ml of water (pH 6-7) at 5°C was given an addition of a solution of 6 mmole of phenyldiazonium chloride, the mixture was stirred at 3-5°C for 3 h and extracted by ether, and the ether extract was washed with a 10% NaOH solution and then with water to a neutral reaction and dried (Na_2SO_4). Evaporation of the solvent yielded 0.34 g (56%) of a substance, which was subjected to column chromatography with elution by a 1:1 benzene–ether mixture. Orange crystals with a decomposition temperature of 180°C and R_f 0.36 (benzene) were obtained. IR spectrum: 3390 (NH), 1400 cm^{-1} (N=N). UV spectrum, λ_{max} (log ε): 203.5 (4.25), 261 (4.49), 300 (4.01), 322 (3.91), 337 nm (3.79). Found: N, 17.0%; M 310. Calculated for $C_{20}H_{14}N_4$: N, 18.0%; M 310. The compound produced a violet color with Ehrlich's reagent at room temperature.

3-(4'-Chlorophenylazo)-1H, 6H-indolo[7, 6-g]indole (VIIIb). A solution of 6 mmole of p-chlorophenyldiazonium chloride was added to a solution of 0.41 g (2 mmole) of I in 50 ml of DMFA and 20 ml of water (pH 7-9) at −5°C, the mixture was stirred at a temperature from −3 to −5°C for 3 h and treated according to the method described above, and 0.43 g of a crude product was obtained (70%). It was purified by column chromatography (the eluent was 1:1 ether–benzene). It was recovered in the form of orange crystals with a decomposition temperature of 270°C and R_f 0.44 (benzene). IR spectrum: 3390, 3410 (NH), 1400 cm^{-1} (N=N). UV spectrum, λ_{max} (log ε): 203 (4.24), 262 (4.60), 335 (4.01), 341 (3.89), 476 nm (4.54). Found: Cl, 10.0; N, 15.7%; M 344. Calculated for $C_{20}H_{13}ClN_4$: Cl, 10.3; N, 16.3%; M 344.5. The compound produced a violet color with Ehrlich's reagent at room temperature.

3-(4'-Nitrophenylazo)-1H, 6H-indolo[7, 6-g]indole (VIIIc). This compound was obtained from 0.41 g (2 mmole) of I and 6 mmole of diazotized p-nitroaniline in analogy to compound VIIIb. The yield of the crude product was 0.35 g (50%). The product was purified in a column (the eluent was 2:1 ether–benzene). It was re-

covered in the form of Bordeaux red crystals with a decomposition temperature equal to 315°C and R_f 0.54 (10:1 benzene–acetone). IR spectrum: 3410, 3340 (NH), 1429 cm^{-1} (N=N). UV spectrum, λ_{max} (log ε): 203.8 (3.87), 260.5 (4.11), 291 (3.63), 526 nm (4.22). Found: N, 19.3%; M 355. Calculated for $C_{20}H_{13}N_5O_2$: N, 19.8%; M 355. The compound produced a violet color with Ehrlich's reagent at room temperature.

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INDOLE DERIVATIVES.

118.* SYNTHESIS OF DERIVATIVES OF PYRROLO[1,2-a]INDOLES ON THE BASIS OF 1-ACETYL-3-INDOLINONE

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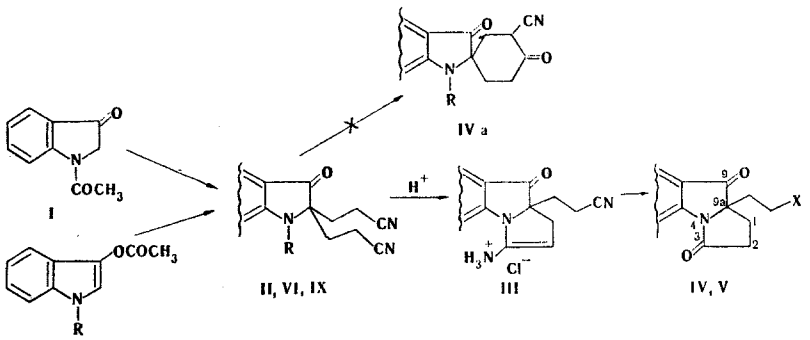
The methods of building up 9-keto-9H-pyrrolo[1, 2-a]indoles on the basis of 1-(o-carboxyphenyl)pyrroles have found application in the synthesis of the antibiotic mitomycin, although they are distinguished by low yields in the cyclization step [2-4].



In the method we propose for constructing the tricyclic system of mytomycin we start out from the condensation product of 1-acetyl-3-indolinone (I) with acrylonitrile, i.e., from 2,2-di-β-cyanoethyl-3-indolinone (II), which is easily cyclized under the action of an ethereal solution of hydrogen chloride to form hydrochloride

*For report 117 see [1].

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