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PYRROLOCARBAZOLES.

4.* ACETYLATION OF 3H-PYRROLO[2,3-c]CARBAZOLE

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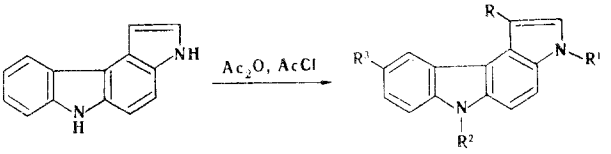
It is shown that 1-acetyl and 1-chloroacetyl derivatives are formed in the Vilsmeier acylation of 3H-pyrrolo[2,3-c]carbazole. The 3,6-diacetyl derivative is formed by the action of Ac_2O without a catalyst, whereas the presence of catalytic amounts of H_3PO_4 leads to 1,6-diacetyl-3H-pyrrolo[2,3-c]carbazole. Only one reaction product, viz., the 9-acetyl derivative, is formed when $AlCl_3$ is used as the catalyst, while a mixture of acylation products was obtained in the presence of $SnCl_4$.

We have previously shown [2] that in the acetylation of 3H-pyrrolo[2,3-c]carbazole with acetic anhydride in the presence of acetic acid the reaction proceeds unambiguously at the carbazole nitrogen atom to give 6-acetyl-3H-pyrrolo[2,3-c]carbazole.

In the present research we made a detailed study of the acetylation of 3H-pyrrolo[2,3-c]carbazole (I) under various conditions.



I II–VI

II $R=COCH_3$, $R^1=R^2=R^3=H$; III $R=COCH_2Cl$, $R^1=R^2=R^3=H$; IV $R^1=R^2=COCH_3$, $R=R^3=H$; V $R=R^2=COCH_3$, $R^1=R^3=H$; VI $R=R^1=R^2=H$, $R^3=COCH_3$

For the synthesis of acetyl derivatives of pyrrolocarbazole I we used the general method of Vilsmeier acetylation with complexes of amides and phosphorus oxychloride.

The use of N,N-diethylchloroacetamide in the reaction with I made it possible to obtain 1-chloroacetyl derivative III in 40% yield. The reaction with N,N-dimethylacetamide proceeds with considerably greater difficulty (II is obtained in 10% yield); this is evidently associated with the smaller degree of electrophilicity of the attacking complex [3].

In the PMR spectra of II and III (Table 1) the absence of the signal of the 1-H proton and the appearance in the strong-field region of characteristic singlets of protons of CH_2 group for II at 2.63 ppm and of a CH_2Cl group for III at 4.96 ppm indicate replacement of the hydrogen atom in the 1 position of the pyrrolocarbazole ring by acetyl and chloroacetyl groups, respectively (i.e., C-acylation).

3H-Pyrrolo[2,3-c]carbazole reacts differently with acetic anhydride than indole to give only an N-acetylation product, viz., 3,6-diacetyl derivative IV, while indole gives a mixture of mono- and diacetyl derivatives [4]. Using orthophosphoric acid as the catalyst we also isolated and characterized 1,6-diacetyl-3H-pyrrolo[2,3-c]carbazole (V).

*See [1] for Communication 3.

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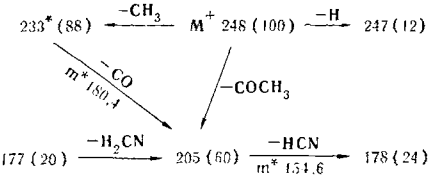
TABLE 1. Chemical Shifts and Spin–Spin Coupling Constants in the PMR Spectra of II-VI*

Compound	δ, ppm										J, Hz
	1-H	2-H	3-H	4-H	5-H	6-H	7-H 8-H 9-H	10-H	$-CH_3$	$-CH_3$	
II	—	8,25	11,9	7,50	7,38	11,2	7,0—7,4	8,60	2,62	—	$J_{23}=3,2$; $J_{45}=8,8$; $J_{910}=7,2$; $J_{810}=2,1$
III	—	8,43	11,4	7,62	7,54	10,5	7,1—7,4	8,64	—	4,96	$J_{23}=3,5$; $J_{45}=8,7$; $J_{910}=7,1$; $J_{810}=1,5$; $J_{710}=0,7$
IV	7,52	8,03	—	8,50	8,24	—	7,4--7,6	8,38	2,72, 2,91	—	$J_{12}=3,8$; $J_{14}=0,5$; $J_{45}=9,3$; $J_{910}=7,3$
V	—	8,35	12,1	7,60	8,20	—	7,2—8,2		2,66, 2,91	—	$J_{23}=2,0$; $J_{45}=9,2$
VI	7,08	7,45	11,3	7,52	7,29	11,5	7,53 (7H), 7,95 (8H)	8,79	2,71	—	$J_{12}=3,3$; $J_{13}=2,2$; $J_{23}=2,5$; $J_{45}=8,7$; $J_{14}=0,5$; $J_{108}=1,6$; $J_{710}=1,0$; $J_{78}=8,5$

*The spectrum of III was obtained from a solution in d_6-acetone, while the spectra of II and IV-VI were obtained from solutions in d_6-DMSO.

In contrast to indole, 3H-pyrrolo[2,3-c]carbazole is readily acetylated under the conditions of the Friedel–Crafts reaction to give monoacetyl-substituted VI, the structure of which was proved by spectral methods. Since pyrrolocarbazole I is a carbazole derivative in which the 3 position of the carbazole ring is blocked by a pyrrole ring, the formation of VI is in complete conformity with the observed principle [5]. The inertness of the pyrrole ring in this reaction is apparently explained by the formation of a complex of aluminum chloride with pyrrolocarbazole I through the pyrrole ring, as a consequence of which the most electron-rich carbon atom in the 9 position in 3H-pyrrolo[2,3-c]carbazole, which corresponds to the 6 position in carbazole, becomes the site of electrophilic attack by the acetylating complex.

The presence of signals of the AB type of the 7-H and 8-H protons with characteristic spin–spin coupling constant (SSCC) J = 8.5 Hz in the PMR spectrum of VI indicates replacement of the hydrogen atom precisely in the 9 position by an acetyl group (Table 1). The 0.6 ppm shift of the signal of the 10-H proton to weak field as compared with the chemical shift of the corresponding proton in unsubstituted heterocycle I (8.19 ppm) is explained by an ortho orientation of the acceptor group relative to the 10-H proton. In contrast to the absorption spectrum of unsubstituted heterocycle I, the UV spectrum of VI is characterized by two absorption bands, viz., one of maximum intensity at 307 nm and one of moderate intensity at 212 nm. The maximum peak in the mass spectrum of VI is the molecular-ion peak (M^+) with m/e 248. The subsequent fragmentation and several fragmentation processes that are confirmed by metastable transitions do not contradict the proposed structure:



When we used $SnCl_4$ as the catalyst, we isolated three compounds with different R_f values and melting points. Two of them, with R_f 0.85 and 0.19, are identical to the substances obtained in the acetylation of pyrrolocarbazole I with acetic anhydride and acetic acid (the 6-acetyl derivative [2]) and with orthophosphoric acid (1,6-diacetyl derivative V). The third product (R_f 0.69) is 9-acetyl-3H-pyrrolo[2,3-c]carbazole (VI). A study of the quantitative composition of the reaction products, which we performed by means of column chromatography, showed that the principal product is VI (34%), while 6-acetyl-3H-pyrrolo-[2,3-c]carbazole and V were obtained in 7 and 4% yields, respectively.

*Here and subsequently, the m/e values are presented along with the relative intensities of the ion peaks in percent of the maximum peak (in parentheses).

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UR spectra of solutions of the compounds in ethanol were obtained with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of the compounds in d_6-DMSO and d_6-acetone were recorded with a Varian CFT-20 spectrometer (80 MHz) with tetramethylsilane as the internal standard. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the substances into the ion source at an ionizing voltage of 50 eV, an accelerating voltage of 2 kV, and a cathode emission current of 1.5 mA.

1-Acetyl-3H-pyrrolo[2,3-c]carbazole (II). A solution of 0.2 g (0.001 mole) of pyrrolocarbazole I in 2 ml of dimethylacetamide was added to a Vilsmeier complex prepared from 0.2 mole of dimethylacetamide and 0.13 ml of phosphorus oxychloride, and the mixture was stirred at 50-60°C for 1 h and allowed to stand overnight. It was then poured into ice water, and the aqueous mixture was made alkaline. The reaction product was purified with a column [silica gel (100/400 μ); the unchanged starting pyrrolocarbazole I was eluted with benzene, while II was eluted with benzene–ether (1:1)] to give 0.024 g (10%) of a product with mp 274-275°C. IR spectrum: 3435, 3390 (NH); 1630 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 229 (4.31), 256 (4.26), 267 (4.22), 297 (4.39), 350 nm (3.67). Found: C 76.9; H 4.6; N 11.2%. $C_{16}H_{12}N_2O$. Calculated: C 77.4; H 4.8; N 11.3%.

1-Chloroacetyl-3H-pyrrolo[2,3-c]carbazole (III). A mixture of 0.3 g (0.002 mole) of $POCl_3$ and 0.3 ml of diethylchloroacetamide was stirred at 20°C for 30 min, and the resulting Vilsmeier complex was cooled and treated with a solution of 0.2 g of I in 3 ml of diethylchloroacetamide. The mixture was stirred at 60°C for 1 h, after which it was cooled and poured into water. The liberated oil was extracted with ethyl acetate, and the extract was washed with sodium carbonate solution and chromatographed with a column [silica gel (100/400 μ), elution with ether] to give 0.11 g (40%) of a product with mp 270-272°C. IR spectrum: 3400, 3430 (NH); 1660 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 220 (4.22); 256 (4.39); 267 (4.33); 302 nm (4.53). Found: C 67.7; H 3.8; Cl 12.1; N 10.0%. $C_{16}H_{11}ClN_2O$. Calculated: C 67.9; H 3.9; Cl 12.6; N 9.9%.

3,6-Diacetyl-3H-pyrrolo[2,3-c]carbazole (IV). A mixture of 0.2 g (0.001 mole) of I and 6 ml of acetic anhydride was refluxed for 2 h, after which it was cooled, and the precipitate was removed by filtration, washed with water, and dried to give 0.23 g (82%) of a product with mp 186-187°C. IR spectrum: 1690, 1710 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 210 (4.67); 263 (4.56); 308 (4.57); 322 (4.51); 333 nm (4.12). Found: C 74.6; H 5.09; N 9.6%. $C_{18}H_{14}N_2O_2$. Calculated: C 74.5; H 4.8; N 9.6%.

1,6-Diacetyl-3H-pyrrolo[2,3-c]carbazole (V). A mixture of 0.2 g (0.001 mole) of I, 4 ml of acetic anhydride, and a few drops of H_3PO_4 was stirred at room temperature for 30 min, after which it was poured into water. The precipitate was removed by filtration, dried, and purified with a column [silica gel (100/400 μ, elution with benzene–ether (1:1)] to give 0.18 g (64%) of a product with mp 235-236°C. IR spectrum: 3155 (NH); 1630 (cm^{-1}). UV spectrum, λ_{max} (log ε): 229 (4.35), 243 (4.42), 284 (4.39), 305 (4.39), 329 nm (4.31). Found: C 74.0; H 5.1; N 9.3%. $C_{18}H_{14}N_2O_2$. Calculated: C 74.5; H 4.8; N 9.6%.

9-Acetyl-3H-pyrrolo[2,3-c]carbazole (VI). A 0.24-ml (0.003 mole) sample of acetyl chloride was added slowly dropwise at 0°C to 0.4 g (0.003 mole) of $AlCl_3$ in 5 ml of methylene chloride, and the resulting complex was stirred for 30 min. A 0.2-g (0.001 mole) sample of pyrrolocarbazole I in methylene chloride was then added at 0°C, and a yellow-green substance gradually began to precipitate. Stirring was continued at the same temperature for 1 h, after which the mixture was decomposed with water and treated with 0.1 ml of HCl. The precipitate was removed by filtration, washed with water, dried, and chromatographed with a column [silica gel (100/250 μ), elution with ethyl acetate–petroleum ether (1:1)] to give 0.15 g (63%) of a product with mp 290-291°C. IR spectrum: 3400, 3390 (NH); 1700 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 212 (4.54), 307 nm (4.71). Found: C 76.9; H 5.1; N 11.1%. $C_{16}H_{12}N_2O$. Calculated: C 77.4; H 4.8; N 11.3%.

Similarly, from 0.2 g (0.001 mole) of I, 0.8 g (0.003 mole) of $SnCl_4$, and 0.24 ml (0.0003 mole) of acetyl chloride we obtained a mixture of substances, which we were able to separate with a column [silica gel (100/250 μ), elution with ethyl acetate–petroleum ether (1:2)]. The yield of VI (R_f 0.69 in ether) was 95 mg (34%), the yield of the 6-acetyl derivative [2] (R_f 0.85 in ether) was 18 mg (7%), and the yield of V (R_f 0.19 in ether) was 10 mg (4%).

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VIBRATIONAL SPECTRA AND STRUCTURES OF THE cis AND trans ISOMERS OF LINEAR BENZINDIGO

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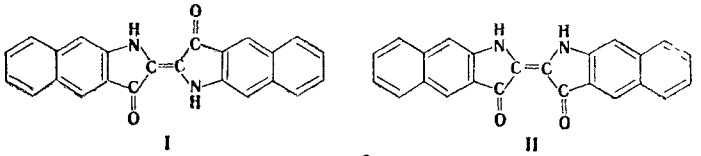
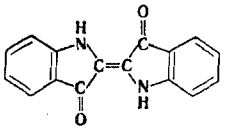
The resonance Raman and IR spectra of the cis and trans isomers of linear benzindigo were investigated, and the frequencies of the vibrations of the multiple bonds were assigned. The large splitting of the frequencies of the symmetrical (ν_s) and asymmetrical (ν_{as}) vibrations of the carbonyl groups of the trans isomer of benzindigo and indigo is associated with the electronic interaction of these groups in the process of vibration.

Recently in the synthesis of 2,3,2',3'-benzindigo the cis isomer (II) was isolated along with the trans isomer (I) [1]. This is evidently the first instance of the isolation of a stable isomer with a cisoid orientation of the carbonyl groups relative to the central double bond of the unsubstituted indigoid chromophore. Thus far, trans-cis photoisomerization of some alkyl and acetyl derivatives of indigo in dilute solutions has been observed; however, when irradiation was discontinued, the small amount of the cis form that was produced was rapidly converted to the more stable trans form.



I

II



III

In the present research we investigated the resonance Raman (RR) and IR spectra of isomers of linear benzindigo and assigned the frequencies of the vibrations of the multiple bonds. For comparison we examined the vibrational spectra of indigo (III), which exists exclusively in the trans form [3].

The nearer absorption band in the electronic spectrum of trans-benzindigo (I) is shifted 72 nm to the long-wave side as compared with the corresponding band of indigo with retention of the contour and approximately the same intensity (Table 1). Thus the added condensed benzene rings make a relatively small contribution to the lower $\pi \rightarrow \pi^*$ transition and a more substantial contribution to the next transition. In the case of cis isomer II

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