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## XVII.* THE CONDENSATION OF 2-AMINOINDOLES WITH ALDEHYDES

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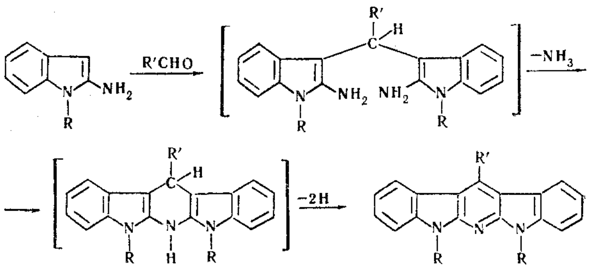
It has been found that the condensation of 1-alkyl-2-aminoindoles with aldehydes forms the previously unknown polycondensed heterocyclic system diindolo[2,3-b:3',2'-e]pyridine.

We have shown previously [1, 2] that the reaction of 1-alkyl-2-aminoindoles with $\beta$-diketones forms $\alpha$-carbolines. Continuing a study of the reactions of 2-aminoindoles with carbonyl compounds, we have found that 2-amino-1-methylindole reacts with benzaldehyde at room temperature in ethanolic caustic potash solution to form a colorless crystalline substance with mp 288-290°C. From its elementary analysis and molecular weight (361), found by mass spectrometry, this substance has the empirical formula $C_{25}H_{19}N_3$, which corresponds to the product of the condensation of two molecules of 2-amino-1-methylindole with one molecule of the aldehyde with the splitting out of one molecule of ammonia, one molecule of water, and two atoms of hydrogen. It was shown by means of Nessler's reagent that ammonia is in fact liberated under the conditions of the reaction (a special experiment showed that the calculated volume of oxygen was absorbed during the process).

The PMR spectrum taken in trifluoroacetic acid characterizes this compound as an aromatic structure with an unresolved aromatic multiplet (7.30 ppm). In the 3.90 ppm region there is a singlet corresponding in intensity to six protons. This can be ascribed to methyl groups attached to the nitrogen atoms of pyrrole rings. Under similar conditions, the condensation of 2-amino-1-methylindole with acetaldehyde gave a substance with mp 265-266°C. Its PMR spectrum is similar to that of the compound obtained from benzaldehyde. An unresolved multiplet with $\delta$ 7.25 ppm corresponds to aromatic protons, and in the strong-field region there are two singlets with a 1 : 2 distribution of intensities (3.07 and 3.80 ppm). All this permits the structure of diindolo[2,3-b:3',2'-e]pyridines to be adopted for the compounds obtained, the formation of which can be represented by the following scheme:



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Then the singlet with $\delta$ 3.07 ppm for 5,7,12-trimethylindolo[2,3-b:3',2'-e]pyridine (I, R = R' = $CH_3$) may be assigned to the methyl group of the pyridine ring, and the singlet with $\delta$ 3.80 ppm to the two methyl groups of the pyrrole rings.

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*For Communication XVI, see [2].

Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 7, pp. 920-922, July, 1970. Original article submitted March 31, 1969.

TABLE 1. Diindolo[2,3-b:3',2'-e]pyridines I

| R | R' | mp, °C | Empirical formula | UV spectra, $\lambda_{max}$, nm (log ε) in triethylamine | Found, % |  | Calc., % |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | C | H | C | H |  |
| $CH_3$ | $CH_3$ | 265—266 | $C_{20}H_{17}N_3$ | 268 (4,31), 295 (4,68), 301 (5,00), 347 (4,18), 359 (4,36), 365 (4,53) | 80,25<br>80,28 | 5,64<br>5,85 | 80,25 | 5,75* | 67 |
| $CH_3$ | $C_6H_5$ | 288—290 | $C_{25}H_{19}N_3$ | 296 (2,60), 303 (2,79), 369 (2,47) | 83,37<br>83,44 | 5,49<br>5,49 | 83,08 | 5,30† | 72 |
| $CH_3$ | 3,4-$(CH_3O)_2C_6H_3$ | 284—288 | $C_{27}H_{23}N_3O_2$ | 295 (2,58), 303 (2,77), 369 (2,48) | 76,75<br>76,98 | 5,74<br>5,76 | 76,55 | 5,51 | 89 |
| $CH_3$ | *p*-$CH_3OC_6H_4$ | 284—286 | $C_{26}H_{21}N_3O$ | 288 (4,53), 296 (4,62), 303 (4,82), 368 (4,38) | 79,53<br>79,76 | 5,56<br>5,67 | 79,77 | 5,41 | 64 |
| $CH_3$ | *p*-$(CH_3)_2NC_6H_4$ | 297—299 | $C_{27}H_{24}N_4$ | 303 (4,90), 368 (4,45) | 80,07<br>80,27 | 6,07<br>6,02 | 80,19 | 5,99 | 77 |
| $CH_3$ | *p*-$ClC_6H_4$ | 314—315 | $C_{25}H_{18}ClN_3$ | 303 (4,87), 364 (4,25) | 75,62<br>75,80 | 4,53<br>4,62 | 75,93 | 4,57 | 81 |
| $CH_3$ | *o*-$ClC_6H_4$ | 310—312 | $C_{25}H_{18}ClN_3$ | 303 (4,90), 348 (4,37) | 75,90<br>75,89 | 4,40<br>4,59 | 75,93 | 4,57 | 66 |
| $CH_3$ | *p*-$BrC_6H_4$ | 328—329 | $C_{25}H_{18}BrN_3$ | 295 (5,36), 303 (5,51), 372 (5,13) | 65,54<br>65,54 | 4,17<br>4,19 | 65,51 | 4,12 | 77 |
| $CH_3$ | *p*-$NO_2C_6H_4$ | 286—288 | $C_{25}H_{18}N_4O_2$ | 295 (4,70), 303 (4,88), 373 (4,51) | 73,80<br>73,80 | 4,45<br>4,48 | 73,84 | 4,46 | 99 |
| $CH_3$ | *m*-$NO_2C_6H_4$ | 345—346 | $C_{25}H_{18}N_4O_2$ | 296 (4,81), 303 (4,85), 373 (4,31) | 73,83<br>73,85 | 4,41<br>4,42 | 73,84 | 4,46 | 79 |
| $C_6H_5CH_2$ | $CH_3$ | 244—246 | $C_{32}H_{25}N_3$ | 302 (5,09), 347 (4,08), 358 (4,38), 365 (4,56) | 85,41<br>85,58 | 5,65<br>5,56 | 84,91 | 5,57 | 55 |
| $C_6H_5CH_2$ | $C_6H_5$ | 288—290 | $C_{37}H_{27}N_3$ | 295 (4,48), 309 (4,64), 368 (4,26) | 86,36<br>86,55 | 5,37<br>5,56 | 86,58 | 5,29 | 98 |

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*Found %: N 14.08, 14.18. Calculated %: N 14.10.

†Found %: N 11.81, 11.94. Calculated %: N 11.63.

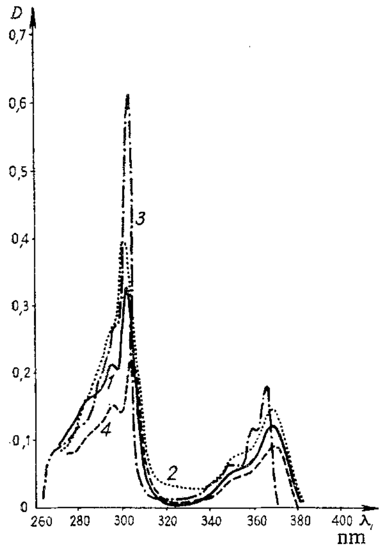

Fig. 1. UV spectra. 1) 12-p-Methoxyphenyl-5,7-dimethyldiindolo[2,3-b:3',2'-e]pyridine; 2) 12-p-dimethylaminophenyl-5,7-dimethyldiindolo[2,3-b:3',2'-e]pyridine; 3) 5,7-dibenzyl-12-methyldiindolo[2,3-b:3',2'-e]pyridine; 4) 5,7-dibenzyl-12-phenyldiindolo[2,3-b:3',2'-e]pyridine.

If the substance $C_{25}H_{19}N_3$ is represented by structure I ($R' = C_6H_5$, $R = CH_3$), the free rotation of the phenyl residue in position 12 will be restricted (because of the propinquity of the protons in positions 1 and 11). This is reflected in the PMR spectrum where, instead of a singlet, the protons of the $C_6H_5$ group are split.

We have synthesized a series of 5,7,12-trisubstituted diindolo[2,3-b:3',2'-e]pyridines (see Table 1), which are colorless crystalline substances, with the exception of the 12-p-dimethylaminophenyl derivative, which is yellow. The substances are high-melting and sparingly soluble in organic solvents, and they possess a deep blue fluorescence in UV light, apart from compounds containing a nitro group.

Chromatography in a thin layer of alumina (activity grade II) in pure benzene gives $R_f$ values for all the substances of from 0.60 to 0.85. Under these conditions, the initial aminoindoles remain at the start.

All the compounds have a characteristic UV spectrum with two main absorption maxima in the 300 and 370 nm region (see Fig. 1 and Table 1). The presence of various substituents in the phenyl group causes only very slight changes in the positions of these maxima.

The similarity of the UV spectra for compounds having $CH_3$ and $C_6H_5$ groups in position 12 and the small influence of substituents in the phenyl ring on the positions of the absorption maxima show a disturbance of coplanarity, as a consequence of which the sextet of $\pi$ electrons of the benzene ring in 5,7-dimethyl-12-phenyldiindolo[2,3-b:3',2'-e]pyridine (I, $R' = C_6H_5$, $R = CH_3$) does not participate in the total conjugation.

## EXPERIMENTAL

Condensation of 2-Aminoindoles with Aldehydes. Caustic potash (2 mmoles), and then, with heating, 2 mmoles of a hydrogen halide salt of a 1-substituted 2-aminoindole were dissolved in 10 ml of ethanol. The hot solution was treated with 2 mmoles of an aldehyde. The flask was filled with inert gas and left at room temperature for 12 h. The crystals that had deposited were filtered off and washed with ethanol. For purification, the substances were dissolved in benzene and the solution was passed through a column (2 × 50 cm) of alumina (activity grade II), the solvent was evaporated in vacuum, and the residue was recrystallized from benzene or from benzene with the addition of ethanol.

The yields and constants of the diindolo[2,3-b:3',2'-e]pyridines are given in Table 1.

## LITERATURE CITED

1. A. N. Kost, R. S. Sagitullin, and V. I. Gorbunov, Dokl. Akad. Nauk SSSR, 184, 835 (1968).
2. A. N. Kost, R. S. Sagitullin, V. I. Gorbunov, and N. N. Modyanov, KhGS [Chemistry of Heterocyclic Compounds] (in press).