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# INTERACTION OF 5-AMINO-2,3-TRIMETHYL-3H-INDOLE WITH p-NITROBENZALDEHYDE

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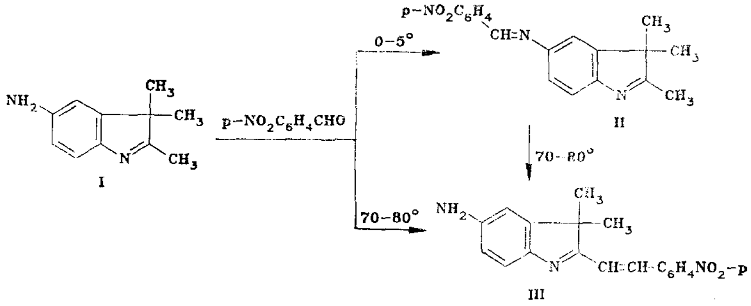
UDC 547.753'571:542.953.4'2

The reaction of 5-amino-2,3,3-trimethyl-3H-indole with p-nitrobenzaldehyde may take place in two directions, depending on the temperature: with the formation of a Schiff's base or of the corresponding styryl compound.

It is known that the reaction of primary amines with aldehydes leads to the formation of Schiff's bases. When 3,3-dibenzyl-2-methyl-3H-indole was heated with benzaldehyde, the corresponding styryl compound was obtained in low yield [1]. We have studied the reaction of p-nitrobenzaldehyde with 5-amino-2,3,3-trimethyl-3H-indole (I) the molecule of which has two reaction centers — the methyl group in position 2 and the amino group. It was found that the reaction took place ambiguously, and its direction depended strongly on the temperature.



The azomethine (II) was formed on the mixing of equimolar amounts of the initial compounds in ethanol at 0-5°C. Heating the initial reactants in boiling ethanol led to 5-amino-3,3-dimethyl-2-p-nitrostyryl-3H-indole (III). Chromatographic monitoring of the latter reaction showed that it took place through the stage of the formation of the azomethine (II), and the styryl compound (III) was the result of thermal rearrangement. This was also confirmed by the fact that heating the azomethine (II) in ethanol led to its conversion into compound (III).

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All-Union State Scientific-Research and Design Institute of the Photographic Chemicals Industry. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1198-1199, September, 1984. Original article submitted October 17, 1983.

## EXPERIMENTAL

The course of the reaction was followed and the purity of the compound was checked on Silufol UV-254. Silica gel (100-250 μ) was used for column chromatography. IR spectra were recorded on a UR-20 spectrometer in KBr tablets; UV spectra on a Hitachi 340 instrument in ethanol; PMR spectra on a Varian XL-100 instrument with $CDCl_3$ as solvent and HMDS as internal standard; and mass spectra on a Varian 311-A MAT instrument with direct introduction of the sample into the ion source at an energy of the ionizing ions of 70 eV.

5-Amino-2,3,3-trimethyl-3H-indole (I). A three-necked flask was charged with 11 g of iron powder, 3 ml of glacial acetic acid, and 40 ml of water. The flask was placed in an oil bath previously heated to 110°C and its contents were stirred for 15 min. Then a hot solution of 10 g (50 mmole) of 2,3,3-trimethyl-5-nitro-3H-indole in 100 ml of ethanol was added to the reaction mixture in portions. The resulting mixture was boiled for 1 h (the end of the reaction was determined chromatographically from the absence of the initial nitroindole), and then 6 g of sodium carbonate was added and stirring was continued for 10 min. The mixture was cooled and the precipitate was filtered off and washed on the filter with hot ethanol. The two filtrates were combined and part of the solvent was distilled off. The precipitate that deposited after cooling was filtered off and recrystallized from aqueous ethanol (2:1). Yield 5.1 g (60%), mp 191-193°C. According to the literature [2]: mp 178°C.

2,3,3-Trimethyl-5-(p-nitrobenzylidene)amino-3H-indole (II). At 0-5°C, 0.58 g (3.3 mole) of the amine (I) in 10 ml of ethanol was added to suspension of 0.5 g (3.3 mole) of p-nitrobenzaldehyde in 10 ml of ethanol. The reaction mixture was kept at the same temperature for 30 min, and then 50 ml of water was added. The precipitate that deposited was filtered off and recrystallized from aqueous ethanol (2:1). Yield 0.83 g (82%), mp 152-154°C. UV spectrum (in ethanol): $\lambda_{max}$ 375 nm (log ε 3.55). IR spectrum: 1630 $cm^{-1}$ (CH=N). PMR spectrum: 2.29 ppm ($2CH_3$), 8.61 ppm (CH=N). Mass spectrum (m/z) (relative intensity, %): 307 (100), 306 (10), 292 (29), 261 (10), 260 (12), 246 (16), 245 (13), 219 (11), 158 (9), 143 (11), 117 (10), 116 (11), 115 (27). Found, %: N 13.4. $C_{18}H_{17}N_3O_2$. Calculated, %: N 13.7.

5-Amino-3,3-dimethyl-2-p-nitrostyryl-3H-indole (III). A. A mixture of 0.75 g (5.0 mmole) of p-nitrobenzaldehyde and 0.87 g (5.0 mmole) of amine (I) in 15 ml of ethanol was boiled for 1.5 h. Then the solvent was driven off and the residue was chromatographed on silica gel with elution by chloroform-acetone (5:1). This gave 0.5 g (33%) of compound (III) with mp 55-56°C, $R_f$ 0.3. UV spectrum (in ethanol): $\lambda_{max}$ 438 nm (log ε 4.33). IR spectrum: 3240 $cm^{-1}$ ($NH_2$). PMR spectrum: 7.39 ppm (CH), 7.67 ppm (CH, J = 16.5 Hz). Mass spectrum, m/z (relative intensity, %): 307 (68), 306 (100), 291 (22), 261 (15), 260 (40), 246 (21), 245 (31), 171 (19), 143 (14), 130 (28), 123 (16), 122 (16), 121 (11), 117 (12), 115 (17). Found, %: N 13.6. $C_{18}H_{17}N_3O_2$. Calculated, %: N 13.7.

B. A solution of 0.5 g (1.8 mmole) of the azomethine (II) in 5 ml of ethanol was boiled for 2 h. Then it was cooled and 15 ml of water was added and the resulting precipitate was chromatographed on silica gel with elution by chloroform-acetone (5:1). This gave 0.35 g (70%) of compound (III), mp 55-57°C, $R_f$ 0.3. A mixture with the sample obtained by method A gave no depression of the melting point.

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