BENZINDOLES

VIII.* NITROSATION IN THE INDOLE AND ANGULAR BENZINDOLE SERIES

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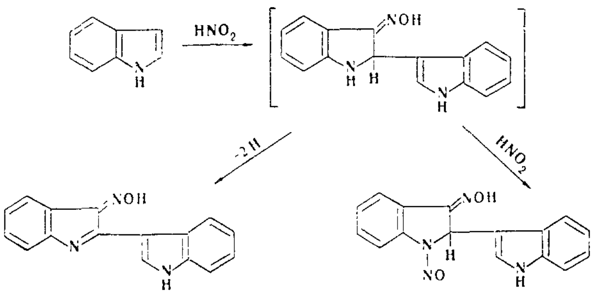
On the basis of the analogy in the PMR spectra of the products of nitrosation of indole and benzindoles it was established that the nitrosation of [4,5]benzindole leads to 1-nitroso-3-oximido-2-([4,5]benzindol-3-yl)-[4,5]benzindoline, while nitrosation of [6,7]benzindoles leads to 3-oximino-2-([6,7]benzindol-3-yl)-[6,7]benzindolenine.

The nitrosation of indoles that have substituents in the pyrrole ring proceeds with the formation of oximido or nitroso compounds, depending on the position of the substituent [2]. In the case of unsubstituted indole the reaction proceeds in a more complex fashion to give two products – the so-called "indole red" (I) and the colorless "dinitroso indole" (II) – the ratio of which depends on the reaction temperature: I is formed primarily at room temperature, while II is formed primarily at 10°C.



I II

In contrast to indole, the reaction of [4,5]- and [6,7]benzindoles with nitrous acid in acetic acid media proceeds unambiguously and, in each case, gives only one product. A colorless substance (III) with R*f* 0.67 [Silufol, benzene–ethanol (6 : 1)] was isolated in the nitrosation of [4,5]benzindole; the dark-red product (IV) of nitrosation of [6,7]benzindole has R*f* 0.34 (with the same system).

The structures of I and II were previously established on the basis of UV spectroscopic data [6] and were confirmed by us by means of the PMR spectra (Table 1). In fact, "dinitrosoindole" form II is characterized by the singlet of an indoline proton (6.42 ppm), and the signal of the indole 2-H proton (7.30 ppm) appears as a doublet ($J_{2,1}$=2.7 Hz). The assignment of this signal was confirmed by double resonance on the signal of the proton of the NH group. The $J_{2,1}$ spin–spin coupling constants are identical for I and II. The PMR spectrum of III also contains the signal of an indoline proton (7.26 ppm), which is absent in the spectra of I and IV. A shift in the signals of the protons of the OH, NH, and 2-H groups to weaker field is

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*See [1] for communication VII.

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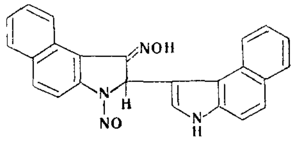
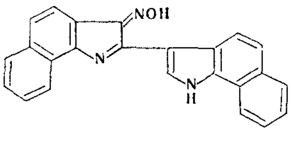
TABLE 1. Chemical Shifts of the Protons of Nitrosoindoles and Nitrosobenzindoles (ppm)

Compound	OH	NH	2-*H*	*H*
I	13,22	11,72	8,26	—
II	11,62	11,01	7,30	6,42
III	11,23	11,35	6,89	7,26
IV	12,69	12,69	8,37	—

observed for the latter as a consequence of an increase in the aromatic character of the entire system, and $J_{2,1}=2.7$ Hz for III, while $J_{2,1}=3.2$ Hz for IV. The chemical shifts of the protons of the OH and NH groups of IV are identical (12.69 ppm), and the integral intensity of this signal corresponds to two protons. These data make it possible to assign a structure similar to II to III and a structure similar to I to IV.



III



IV

The formation of I and II should proceed through an intermediate, which, on the one hand, is, in all likelihood, oxidized by nitrogen oxide to I, and, on the other, is nitrosated further to II. The absence of compounds similar to I in the products of nitrosation of [4,5]benzindole attests to the relative stability of the intermediate with respect to oxidation. In the case of [6,7]benzindole, the formation of IV proves to be preferable, apparently as a consequence of steric hindrance during nitrosation at nitrogen.

EXPERIMENTAL

The PMR spectra of dimethyl sulfoxide solutions were recorded with an HA-100 spectrometer with hexamethyldisiloxane (HMDS) as the internal standard. The IR spectra of mineral-oil suspensions were recorded with a UR-10 spectrometer.

1-Nitroso-3-oximido-2-([4,5]benzindol-3-yl)-[4,5]benzindoline (III). A 1.7-g sample of [4,5]benzindole was suspended in 15 ml of glacial acetic acid, and a solution of 0.65 g of $NaNO_2$ in 1 ml of water was added to it gradually. The mixture was stirred at room temperature for 4 h and poured into 200 ml of water. The resulting precipitate was removed by filtration, washed with water, and dried in a vacuum desiccator over NaOH to give 1.9 g (quantitative) of III. The product was recrystallized from ethyl acetate to give barely yellowish crystals (the melting point was not determined). Found: C 73.1; H 4.1; N 14.3%. $C_{24}H_{16}N_4O_2$. Calculated: C 73.5; H 4.1; N 14.3%. IR spectrum: 3410, 3335, and 1710 cm^{-1}. UV spectrum (in ethanol), λ_{max}, nm (log ε): 250 (4.42), 290 (4.10), 300 (4.10), 316 (3.98), and 330 (3.92).

3-Oximido-2-([6,7]benzindol-3-yl)-[6,7]benzindoline (IV). The nitrosation was carried out by the method described for [4,5]benzindole to give 1.45 g (quantitative) of IV from 1.3 g of [6,7]benzindole and 0.5 g of $NaNO_2$. Recrystallization from alcohol gave a dark-red crystalline substance (the melting point was not determined). Found: C 76.5; H 4.2; N 11.3%. $C_{24}H_{15}N_3O$. Calculated: C 76.4; H 4.0; N 11.1%. IR spectrum: 3420, 1680, and 1630 cm^{-1}. UV spectrum (in ethanol), λ_{max}, nm (log ε): 268 (4.38) and 284 (4.31).

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