S. I. Bobrovskii, E. V. Babaev, and Yu. G. Bundel

UDC 547.759

By PMR spectroscopy we showed that 2-methyl-1-nitro- and 2-methyl-3-nitroindolizines are protonated in an acidic medium at position 3, giving the corresponding 3H-indolizinium cations.

Like the PMR spectra of alkylindoliziniums [1], the spectrum of the cation (I) in sulfuric acid contains the signal for the methylene group at  $\delta$  5.63 s (2H, CH<sub>2</sub>) ppm, in addition to the resonance signals of the pyridine fragment. In solution in D<sub>2</sub>SO<sub>4</sub> a slow decrease is observed in the integral intensity of the singlet (CHD) as a result of acid deuteroexchange. In the case of the cation (II) the C<sup>3</sup>H singlet (7.50 ppm), which appears in H<sub>2</sub>SO<sub>4</sub>, is absent in D<sub>2</sub>SO<sub>4</sub>; here the intensity of the C<sup>1</sup>H singlet (7.40 ppm) slowly decreases.\* In trifluoroacetic acid 2-methyl-3-nitroindolizine is present in the neutral form, whereas the more basic l-isomer is protonated almost completely. We note that the possibility of ipso-protonation in relation to the NO<sub>2</sub> group was demonstrated earlier [3] for the case of 4,6,8-trimethyl-1-nitroazulene [3].

## LITERATURE CITED

- 1. M. Fraser, A. Melera, B. B. Molloy, and D. H. Reid, J. Chem. Soc., 1962, No. 9, 3288-3294.
- 2. W. Engewald, C. Weiss, and M. Muhlstadt, Isotopenpraxis, 4, No. 8, 326-328 (1968).
- 3. J. Schulze and F. A. Long, Proc. Chem. Soc., 1962, No. 11, 364-365; J. Am. Chem. Soc., 86, No. 3, 322-326 (1964).
- \*Acid deuteroexchange at position 1 of 3-nitroindolizine was observed earlier [2].

M. V. Lomonosov Moscow State University. Translated from Zhurnal Organicheskoi Khimii, Vol. 21, No. 3, p. 673, March, 1985. Original article submitted June 4, 1984.