PROTONATION OF 2-METHYL-1-NITRO- AND 2-METHYL-3-NITROINDOLIZINES

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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 \( \delta 5.63 \) (2H, CH\(_2\)) ppm, in addition to the resonance signals of the pyridine fragment. In solution in D\(_2\)SO\(_4\), 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\(^3\)H singlet (7.50 ppm), which appears in H\(_2\)SO\(_4\), is absent in D\(_2\)SO\(_4\); here the intensity of the C\(^1\)H singlet (7.40 ppm) slowly decreases.* In trifluoroacetic acid 2-methyl-3-nitroindolizine is present in the neutral form, whereas the more basic 1-isomer is protonated almost completely. We note that the possibility of ipso-protonation in relation to the NO\(_2\) group was demonstrated earlier [3] for the case of 4,6,8-trimethyl-1-nitroazulene [3].

LITERATURE CITED


*Acid deuteroexchange at position 1 of 3-nitroindolizine was observed earlier [2].