ipso-PROTONATION OF 2-METHYL-3-PIVALOYLINDOLIZINE

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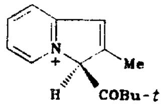
We have found for the first time ipso-protonation of acylhetarenes from 2-methyl-3-pivaloylindolizine I via formation of the 3H-indolizine cation II* in CF_3COOH



II

When compared with starting indolizine I the PMR spectrum of cation II showed low field shifts for protons 1, 6, 7, and 8 but a high field shift (from 8.75 to 8.30 ppm) for proton 5. The latter was a result of the derivation from the heterocyclic plane at the position peri to the magnetically anisotropic acyl group. The signals for the 3-H (ipso) and 1-H protons were seen at 6.90 and 6.80 ppm, respectively, in CF_3COOH but did not appear in CF_3COOD solution. Similar spectral changes have been reported by us previously upon ipso-protonation of 2-methyl-3-nitroindolizine [1]. Compound I was obtained in 55% yield from 2-methylindolizine and t-BuCOCl and has elemental analytical data in agreement with that calculated. We are at present investigating the course of protonation and the basicity of a wide range of 3-substituted indolizines.

LITERATURE CITED

1. S. I. Bobrovskii, E. V. Babaev, and Yu. G. Bundel', Zh. Org. Khim., 21, 673 (1985).

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*A significant chromatographic mobility was noted for the trifluoroacetate of II (R_f 0.50, silufol, hexane-ethyl acetate 5:1).

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