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LETTERS TO THE EDITOR

INDOLIZINOPHANE - A NEW TYPE OF HETEROPHANE

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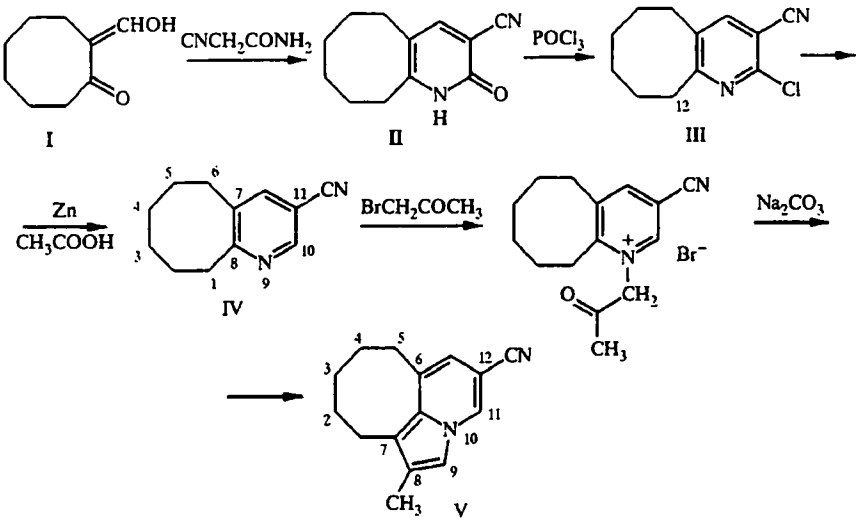
The first examples have been obtained of indolizinophanes V, in which a polymethylene chain is bonded to the pyridine and pyrrole rings of the molecule. The pyridinophane starting material IV was obtained by condensation of α-hydroxymethylenecyclooctanone (I) with cyanoacetamide, followed by chlorination of the pyridone II and dechlorination of the 2-chloro derivative III into the pyridinophane IV. Compound IV was then converted into 8-methyl-12-cyano-[5](1,8)-indolizinophane (V) by the Chichibabin reaction as shown in the following scheme:



The indolizinophane V is an example of a new type of heterophane.

11-Cyano[6](2,3)-pyridinophan-10-one (II) was obtained by heating a mixture α-hydroxymethylenecyclooctanone (I) (5.18 g, 33.6 mmole), aqueous ethanol (45 ml), cyanoacetamide (2.84 g, 46.3 mmole), and piperidine (1 ml) at 60°C for 5 h. The precipitate was filtered off and washed with cold methanol to give compound II (4.92 g, 71%), m.p. 219-221°C (from ethanol). ^{1}H NMR Spectrum (DMSO-d_6): 1.34-1.63 (8H, m, CH_2), 2.56-2.73 (4H, m, CH_2), 8.10 (1H, s, 12-H), 12.23 ppm (1H, s, NH).

10-Chloro-11-cyano-[6](2,3)-pyridinophane (III). A mixture of compound II (1.47 g, 7.3 mmole), PCl_5 (0.74 g, 3.7 mmole) and $POCl_3$ (5.5 ml) was heated at 100°C for 5 h, poured onto ice, and the precipitate filtered off to give compound III (1.19 g, 74%), m.p. 91-92°C (from hexane). ^{1}H NMR Spectrum ($CDCl_3$): 1.40-1.83 (8H, m, CH_2), 2.77-2.83 (2H, m, CH_2), 2.96-3.02 (2H, m, CH_2), 7.79 ppm (1H, s, 12-H).

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11-Cyano-[6](2,3)-pyridinophane (IV). A solution of compound III (1.63 g, 7.4 mmole) in a mixture of acetic acid (12 ml) and aqueous ethanol (2:1, 18 ml) was heated to boiling. Zinc powder (1.94 g, 2.96 mmole) was then added in portions and the mixture was heated for a further 1.5 h to give compound IV as a colorless oil (1.17 g, 85%). ^{1}H NMR Spectrum ($CDCl_3$): 1.38-1.40 (8H, m, CH_2), 1.75-1.83 (4H, m, CH_2), 7.68-7.69 (1H, d, J = 2.0 Hz, 12-H), 8.66-8.67 ppm (1H, d, 10-H). Mass spectrum, *m/z*: 186 [M^+].

8-Methyl-12-cyano-[5](1,8)-indolizinophane (V). A mixture of compound IV (0.60 g, 3.3 mmole) and bromoacetone (0.90 g, 6.6 mmole) in the minimal volume of acetone was boiled for 6 h. The solvent was evaporated, the residue was dissolved in ethanol (5 ml), Na_2CO_3 was added and the mixture was boiled for 1 h to give compound V (0.48 g, 65%), m.p. 134-135°C (from hexane). ^{1}H NMR Spectrum ($CDCl_3$): 1.36-1.85 (8H, m, CH_2), 2.20-2.21 (3H, d, J = 0.6 Hz, CH_3), 2.99-3.06 (4H, m, CH_2), 6.26-6.27 (1H, m, 11-H), 7.12-7.13 (1H, m, 7-H), 8.06-8.07 ppm (1H, d, J = 1.4 Hz, 9-H). IR Spectrum: 2230 (CN), 2850-2940 (—CH_2—), 3010 cm^{-1}.

Elemental analysis results agreed with calculated values.

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