

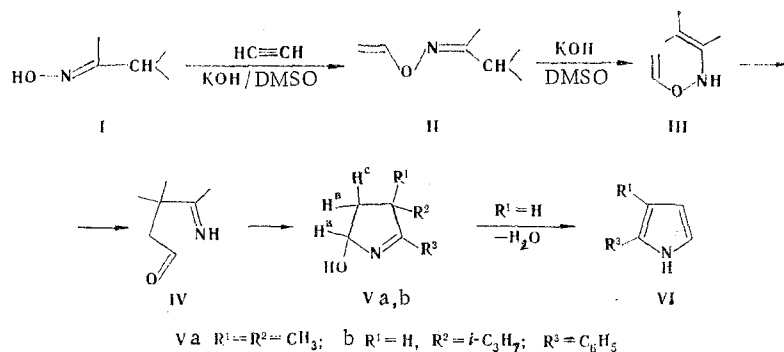
4H-2-HYDROXY-2,3-DIHYDROPYRROLES — INTERMEDIATES IN THE FORMATION OF PYRROLES
FROM KETOXIMES AND ACETYLENE IN THE KOH-DMSO SYSTEM

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UDC 547.574.2:547.314.2:547.743.1:542.952

One of the possible methods for the formation of pyrroles from ketoximes I and acetylene in the KOH-DMSO superoxide catalytic system is the heteroatomic variant of the Claisen rearrangement of intermediate vinyloxy imine II, which undergoes prior prototropic isomerization to O,N-divinylhydroxylamine (III) [1]. However, despite the fact that it has long been possible to isolate vinyloxy imines II from the reaction products [2] and in some cases [3] to demonstrate their ability to undergo conversion to pyrroles under the influence of a superbase (KOH-DMSO), the proposed intermediate steps in the rearrangement have not yet been proved.

We here report for the first time the successful interruption of a reaction, discovered and developed by us, at the step involving the formation of 4H-2-hydroxy-2,3-dihydropyrroles (Va, b) — representatives of the heretofore unknown class of five-membered nitrogen heterocycles.



The pyrolysis of vinyloxy imines II in the absence of KOH-DMSO does not lead to V [according to gas-liquid chromatography (GLC)].

4H-4,4-Dimethyl-2-hydroxy-5-phenyl-2,3-dihydropyrrole (Va), with mp 108–110°C (from 50% alcohol), was obtained from isopropyl phenyl ketone oxime in 21% yield; the mass spectrum contained M⁺ peaks with m/z 189, and the results of elementary analysis were in agreement with the formula. PMR spectrum (CDCl₃): 7.57 (Ph), 6.90 (OH), 5.77 (t, a-H), 2.24 (q, b-H), 1.84 (q, c-H), 1.36 and 1.38 ppm (CH₃); J_{a(b,c)} = 6.25, J_{ab} = 6.0, J_{ac} = 6.5, J_{bc} = 12.75 Hz. IR spectrum: 1102, 3176, 3400 (OH); 1614 (C=N); 1574 (Ph); 1328, 1445, 2870, 2964 cm⁻¹ (CH₃, CH₂). UV spectrum, λ_{max} (log ε): 202 (4.37) and 241 nm (4.0).

4H-2-Hydroxy-2,3-dihydropyrrole Vb (R¹ = H) (mp 133–134°C), which was obtained in 26% yield from isobutyl phenyl ketone oxime and was converted to pyrrole VI upon storage and heating, had similar spectral characteristics.

LITERATURE CITED

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskih Soedinenii, No. 2, pp. 276–277, February, 1983. Original article submitted August 16, 1982.