THE CONTRIBUTION OF TERTIARY HYDROGEN IN THE BOHLMANN ABSORPTION REGION

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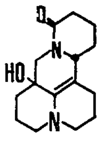
UDC 547.944/945

In view of the fact that in the IR spectrum of 5-hydroxy-6,7-dehydromatrine (I), and 5,6-dehydrosparteines the trans band is absent, the hypothesis has been put forward that a tertiary hydrogen atom makes the greatest contribution to this region of the IR spectra of trans-quinolizidines [1].

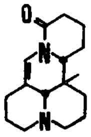
The introduction of a double bond into the cyclohexane ring leads to the deviation of the α bonds from their original positions into the "pseudoaxial" and "pseudoequatorial" positions [2].

We assume that the same effect is possible in the case of (I), and, therefore, the trans-diaxial mutual arrangement of the lone electron pair of the nitrogen atom and of the adjacent hydrogen atoms is disturbed. It is probably as a result of this that no trans band is observed in the IR spectrum of (I). This hypothesis could be confirmed by recording the IR spectrum of a compound in the trans-quinolizidine linkage of which there is an α, β double bond and the α (to the nitrogen) tertiary hydrogen atom is retained.

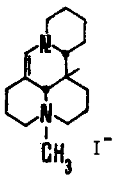
Using the method described by Bohlmann et al. [3] we have obtained 5,17-dehydroallomatrine (II); in its C/D linkage the double bond does not affect the tertiary α-hydrogen atom. The nitrogen of the A/B linkage of (II) was blocked by the formation of the methiodide derivative. A methiodide with mp 248-249°C was isolated from the reaction mixture, and this was reduced with lithium tetrahydroaluminate in absolute ether by a published method [4].



I



II



III

Absorption bands were completely absent from the 2800–2700-cm^{-1} region in the IR spectrum of the reduction product (III).

The results obtained show that in the spectra of α,β-unsaturated derivatives of trans-quinolizidine no absorption bands are found in the 2800–2700-cm^{-1} region even when a tertiary α (to the nitrogen) hydrogen atom is retained, and thus it is impossible to ascribe the major contribution in the region of the trans bonds to it.

It is likely that in the α,β-unsaturated derivatives of trans-quinolizidine, as a result of the deformation of the ring, the trans-diaxial mutual arrangement of the lone electron pair of the nitrogen atom and of the adjacent hydrogen atoms is disturbed and, consequently, no absorption in the Bohlmann region is observed in the IR spectra.

V. I. Lenin Tashkent State University. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 809-810, November-December, 1972. Original article submitted February 23, 1972.

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