BOHLMANN ABSORPTION IN THE IR SPECTRA OF STRAINED trans-FUSED PYRROLIZIDINES

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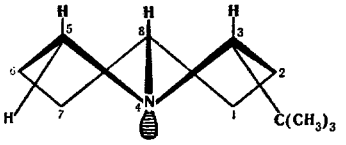
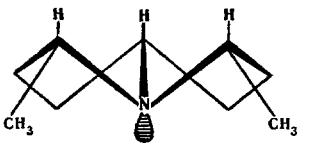
For the first time we have observed Bohlmann absorption [1] for systems with two strained trans-fused five-membered rings and a nodal nitrogen atom in the case of pyrrolizidines I [2] (2692 m, 2712 sh, and 2742 sh cm^{-1}) and II [3] (2700 m, 2715 w, 2743 w, and 2760 w cm^{-1}).

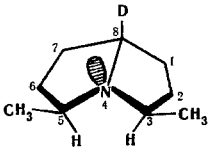


I

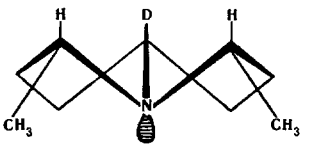


II

In both cases the alkyl groups occupy pseudoequatorial positions. The role of the 8-H atom in the appearance of Bohlmann absorption was shown by direct introduction of a deuterium label in the 8 position. Isomers III (ν_{C-D} 2125, 2150 cm^{-1}) and IV (ν_{C-D} 1958, 1992, and 2034 cm^{-1}) were obtained by catalytic deuteration of cis-3,5-dimethyl-$\Delta^{4(8)}$-dehydropyrrolizidinium perchlorate. The most intense bands of the isomers (indicated by bold type) differ in frequency by more than 130 cm^{-1}. The shift of ν_{C-D} to the low-frequency region on passing from isomer III to isomer IV is due to a change in the character of the mutual orientation of the unshared pair of nitrogen and the C–D bond.



III



IV

These data constitute a rare and clear illustration of the dependence of ν_{C-D} on the conformation of the isomeric compounds. Compounds I-IV may supplement a series of models for the study of the limits of the effect of Bohlmann absorption.

The IR spectra of thin layers of the liquids were recorded with UR-10 and UR-20 spectrometers with an LiF prism.

LITERATURE CITED

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2. I. M. Skvortsov, I. V. Antipova, Yu. A. Pentin, Tran Suan' Khoan', and S. V. Vasil'kovskii, Khim. Geterotsikl. Soedin., No. 8, 1087 (1975).
3. I. M. Skvortsov, I. V. Antipova, G. P. Mal'chenko, and K. S. Ovchinskii, in: Problems in Stereochemistry [in Russian], Vol. 4 (1974), p. 41.

N. G. Chernyshevskii Saratov State University. M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1001-1002, July, 1976. Original article submitted December 29, 1975.