

## LETTERS TO THE EDITOR

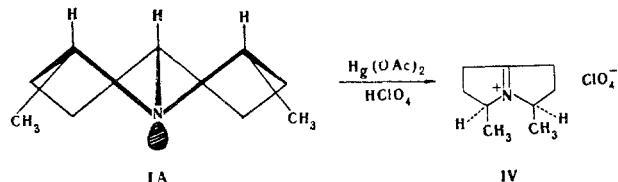
DETECTION OF THE *trans*-FUSED CONFORMATION  
OF THE PYRROLIZIDINE SKELETON IN *cis*-3,8-H-3-  
METHYL-*cis*-5,8-H-5-METHYL PYRROLIZIDINE

I. M. Skyortsov and A. M. Plotnikov

UDC 547.759.5:541.634

The oxidative dehydrogenation of saturated bicyclic bases with an angular nitrogen atom with mercuric acetate [1, 2] occurs only in the case of an anticoplanar orientation of the unshared electron pair of the nitrogen atom and the C—H bond of the  $\alpha$ -carbon atom common to the two rings [3], i.e., in the case of trans-fused rings. The behavior of various bases in this reaction has been used to make stereochemical assignments [4]. Pyrrolizidine is inert with respect to mercuric acetate [4], and this is in agreement with the concept of cis fusion of its rings.

We have examined the oxidation of a mixture of *cis*-3,8-H-3-methyl-*cis*-5,8-H-5-methylpyrrolizidine (I) (39%), *cis*-3,8-H-3-methyl-*trans*-5,8-H-5-methylpyrrolizidine (II) (52%), and *trans*-3,8-H-3-methyl-*trans*-5,8-H-5-methylpyrrolizidine (III) (9%), prepared by catalytic hydrogenation of 3,5-dimethyl-1,2-dihydropyrrolizine. The reaction with mercuric acetate was carried out as in [1]. At the end of the reaction, the mixture of bases had the following composition, according to gas-liquid chromatography (GLC): 7% I, 85% II, and 8% III. Thus isomer I is more active in the reaction than the other isomers; we feel that this is linked with its ability to take on *trans*-fused form IA as a result of liberation from the strong nonbonded interactions in the *cis*-fused conformations. The concentration of IA in an equilibrium mixture of the conformations of isomer I should be relatively high in order to insure relatively rapid reaction [the first crystals of  $Hg_2(OAc)_2$  appear after 5 min, and the reaction time is 2.5 h] but of the same order as observed under similar conditions in the dehydrogenation of *trans*-fused quinolizidine [1] and indolizidine [2].



The isolation of *cis*-3,5-dimethyl- $\Delta^4$ (8)-dehydropyrrolizidinium perchlorate [IV, mp 211.5-214° [dec., from ethanol-ether (1:1)]] from the reaction mixture constitutes evidence, according to [3], that it originates from IA. The  $C=N^+$  multiple bond in salt IV is detected from its characteristic band at  $1674\text{ cm}^{-1}$

[2], and its position is unambiguously determined by the magnetic equivalence of the methyl groups in the PMR spectrum. PMR spectrum (60 MHz, 0.35 M solution in D<sub>2</sub>O, sodium 4,4-dimethyl-4-silapentane-1-sulfonate internal standard),  $\delta$ , ppm: 3-H and 5-H 4.42 (multiplet), 1-CH<sub>2</sub> and 7-CH<sub>2</sub> 2.94 (multiplet), 2-CH<sub>2</sub> and 6-CH<sub>2</sub> 1.8-2.8 (multiplet), and 3-CH<sub>3</sub> and 5-CH<sub>3</sub> 1.49 (doublet,  $J$ =6.5 Hz); the signal intensity ratio is 1:2.1:2.3:3.2.

#### LITERATURE CITED

1. N. J. Leonard, A. S. Hay, R. W. Fulmer, and V. W. Gash, *J. Amer. Chem. Soc.*, 77, 439 (1955).
2. N. J. Leonard, W. J. Middleton, P. D. Thomas, and D. Choudhury, *J. Org. Chem.*, 21, 344 (1956).
3. N. J. Leonard and D. F. Morrow, *J. Amer. Chem. Soc.*, 80, 371 (1958).
4. F. Bohlmann and C. Arndt, *Ber.*, 91, 2167 (1958).

N. G. Chernyshevskii Saratov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii. No. 7, pp. 1003-1004, July, 1975. Original article submitted October 3, 1974.

©1976 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.