

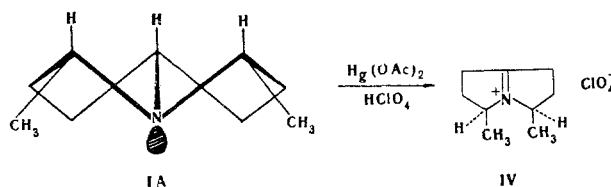
DETECTION OF THE *trans*-FUSED CONFORMATION
OF THE PYRROLIZIDINE SKELETON IN *cis*-3,8-H-3-
METHYL-*cis*-5,8-H-5-METHYLPYRROLIZIDINE

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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 α -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 $\text{Hg}_2(\text{OAc})_2$ 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 $\text{C}=\text{N}^+$ multiple bond in salt IV is detected from its characteristic band at 1674 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_2O , sodium 4,4-dimethyl-4-silapentane-1-sulfonate internal standard), δ , ppm: 3-H and 5-H 4.42 (multiplet), 1- CH_2 and 7- CH_2 2.94 (multiplet), 2- CH_2 and 6- CH_2 1.8–2.8 (multiplet), and 3- CH_3 and 5- CH_3 1.49 (doublet, $J=6.5$ Hz); the signal intensity ratio is 1:2.1:2.3:3.2.

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