

BOAT-CHAIR EQUILIBRIUM IN A 4-PIPERIDINOL

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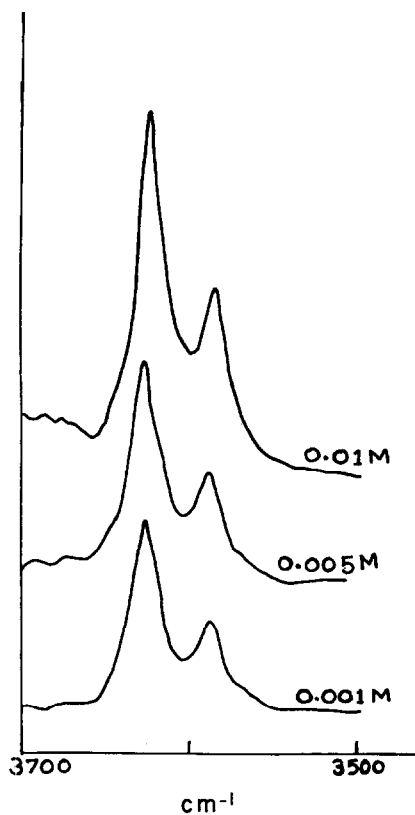
WE recently reported<sup>1</sup> the reduction of some substituted 4-piperidones leading to pairs of epimeric 4-piperidinols, designated as  $\alpha$ - and  $\beta$ -forms. The  $\alpha$ - and  $\beta$ -forms were also shown to have an equatorial and an axial hydroxyl group, respectively, in the chair form of the piperidine ring. We have now examined the infrared spectra of two pairs of the piperidinols in dilute carbon disulphide solution at concentrations of 0.01, 0.005 and 0.001 mole per litre.

The infrared spectra of the  $\alpha$ - and  $\beta$ -forms of 1-methyl-2,6-diphenyl-4-piperidinol (I  $\alpha$ , m.p. 163-164° and I  $\beta$ , m.p. 170-172°) and 1,3,5-trimethyl-2,6-diphenyl-4-piperidinol (II  $\alpha$ , m.p. 133-134° and II  $\beta$ , m.p. 99-100°) showed that except for II  $\alpha$  the other piperidinols gave a single band in the O-H stretching region due to unbonded hydroxyl (I  $\alpha$  3607 cm.<sup>-1</sup>, I  $\beta$  3612 cm.<sup>-1</sup>, II  $\beta$  3630 cm.<sup>-1</sup>). In contrast, II  $\alpha$  gave two bands in the region at 3626 cm.<sup>-1</sup> and 3587 cm.<sup>-1</sup> (see Fig. 1). The relative intensity of these bands was independent of concentration, which showed that the low frequency band is due to intramolecular hydrogen bond between the hydroxyl group and the nitrogen atom of the ring. Since a band

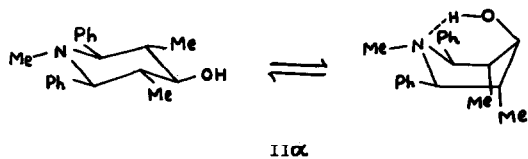
<sup>1</sup> M. Balasubramanian and N. Padma, Tetrahedron Letters No. 14, 23 (1960).

FIG. 1

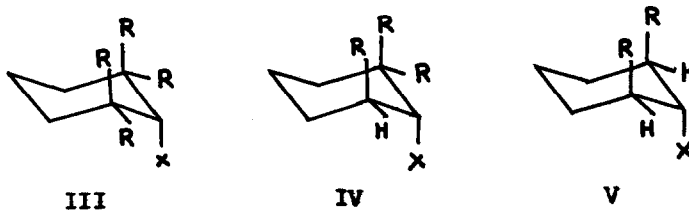
IR spectra of 1,3,5-trimethyl-2,6-diphenyl-4-piperidinol,  $\alpha$ -form in  $\text{CS}_2$



due to unbonded hydroxyl also appears,  $\text{II}\alpha$  should exist as an equilibrium mixture of the chair and the boat conformations.



The  $\alpha$ -form of 1-methyl-2,6-diphenyl-4-piperidinol ( $I\alpha$ ) is also capable of intramolecular hydrogen bond formation in the boat conformation. The presence of such an interaction in only  $I\alpha$  is interesting. An examination of the non-bonded interactions in the chair and the boat form of the piperidinols leads to a probable explanation. Barton<sup>2</sup> has shown that in a 2,2,6,6-tetrasubstituted cyclohexane derivative (III) the substituent X is more stable in the axial than in the equatorial orientation. It was also predicted<sup>3</sup> that this reversed order of stability



should hold for IV and V as well, the rings being anchored in a single chair form. Examples of type V are provided in tropane alkaloids (2,6-diaxially substituted piperidines) where Fodor and co-workers<sup>4-6</sup> have shown that an axial orientation is favoured for the N-alkyl group.

In the chair conformation of  $I\alpha$  the presence of two equatorial methyl groups adjacent to the hydroxyl introduces non-bonded 1,2-interactions which are absent in  $I\alpha$  or  $I\beta$ . The axial-like orientation of the two methyl and the hydroxyl groups in the boat form of  $I\alpha$  relieves

<sup>2</sup> D.H.R. Barton, Chem. & Ind. (Rev.) 664 (1953).

<sup>3</sup> D.H.R. Barton and R.C. Cookson, Quart. Rev. Chem. Soc., Lond. 10, 79 (1956).

<sup>4</sup> G. Fodor, K. Koczka and J. Lestyán, J. Chem. Soc. 1411 (1956).

<sup>5</sup> G. Fodor, J. Tóth and I. Vincze, J. Chem. Soc. 3504 (1955).

<sup>6</sup> O. Kovács, G. Fodor and M. Halmos, J. Chem. Soc. 873 (1956).

these interactions. This form is also stabilised by hydrogen bond formation. However, it has unfavourable 1,3-interaction between the two methyl groups. Thus it appears that the energy barrier between the chair and the boat conformations is rather low in this piperidinol.

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