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# THE PREPARATION AND THE CONFIGURATION OF SOME STEREOISOMERIC CARANYLAMINES

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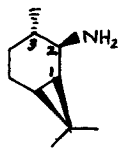
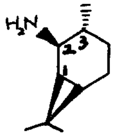
In view of a recent publication[1] on the configuration and conformation of (+)-*trans*-caranyl-*cis*-2-amine (I)[2,3] we wish to report our preparations of the six stereoisomeric caranylamines (II-VII) by routes summarised in the chart below.



I



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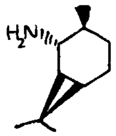

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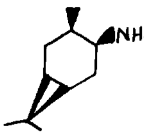

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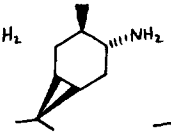

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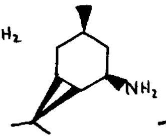

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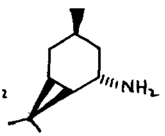
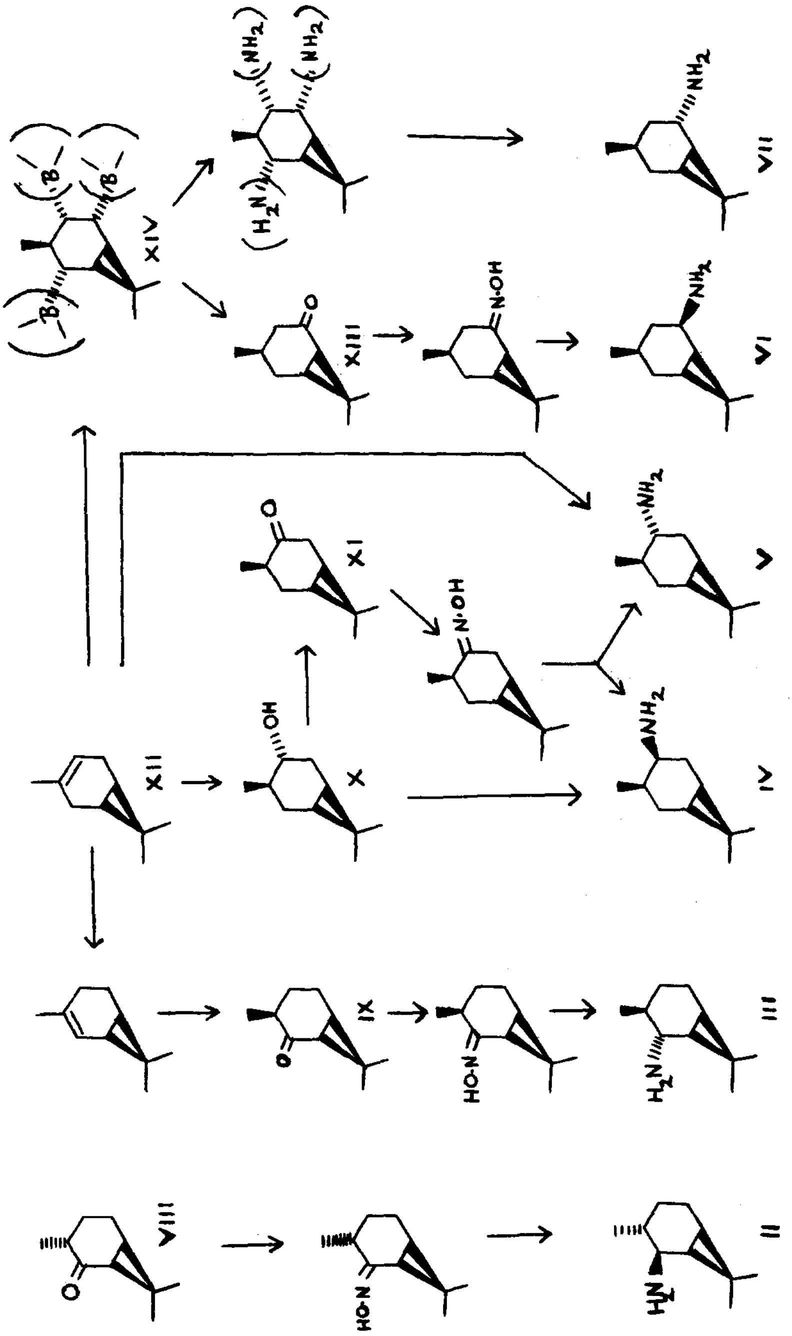


VII

The preparation of (-)-*trans*-caranyl-*cis*-2-amine (II) was achieved essentially by previously used methods,[1,2,3] namely by reduction of the oxime of (-)-*trans*-caran-2-one (VIII)[4] with sodium in ethanol. A similar procedure with the oxime of (-)-*cis*-caran-2-one (IX)[4] gave (-)-*cis*-caranyl-*trans*-2-amine (III). (+)-*cis*-Caranyl-*cis*-4-amine (IV) was prepared by two routes. (a) The tosylate of (-)-*cis*-caran-*trans*-4-ol (X)[4] was converted to the inverted azide which was reduced with lithium aluminium hydride to the amine (IV). (b) The oxime of (-)-*cis*-caran-4-one (XI)[4] was hydrogenated over Adams catalyst giving predominantly the same amine (IV). The epimeric (-)-*cis*-caranyl-*trans*-4-amine (V) was obtained from the oxime of (-)-*cis*-caran-4-one (XI)[4] by reduction with sodium in ethanol. This amine (V) was also obtained by the aminative hydroboronation of (+)-car-3-ene (XII).[5] (+)-*cis*-Caranyl-*cis*-5-amine (VI) was prepared by reduction of the oxime of (+)-*cis*-caran-5-one (XIII)[6] with sodium in ethanol. The epimer (-)-*cis*-caranyl-*trans*-5-amine (VII) was formed as the main product of the amination of the


XIV
XIII
XII
XI
X
IX
VIII
VII
VI
V
IV
III
II
NH$_2$
H$_2$N
N·OH
HO-N
OH
O
B

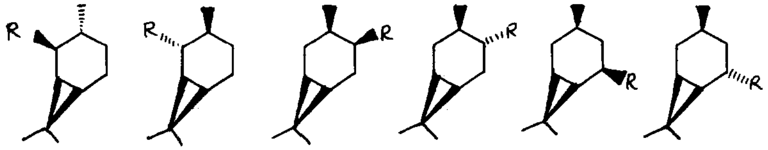
mixture of cis-caranyl-trans-boranes (XIV) derived by thermal equilibration at 100° of cis-caranyl-trans-4-borane.[6]

Each amine (II-VII) was purified through an appropriate salt.

Detailed evidence for the configurations and conformations of the amines (II-VII) will be given in a paper now being prepared, but attention may here be drawn to a comparison of the optical rotations of the amines and the corresponding alcohols (Table)

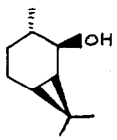
TABLE

Comparison of the Optical Rotations of the Amines (II) - (VII) and
the Corresponding Alcohols

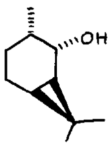


| | | | | | | |
|---|---|---|---|---|---|---|
| R = $NH_2$ | -58.5° | -30.5° | +27.3° | -77.1° | +52.3° | -29.5° |
| R = OH | -54° | -34° | +4.9° | -73.2° | -45.7° | -22.9° |

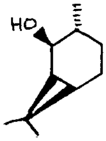
There is good correlation between the optical rotations of the above amines and the corresponding alcohols. The discrepancy in the case of the amine (IV) is explained by a partial conformational change for which supporting evidence will be given later. The large discrepancy in the values recently published[1] for the (+)-caranylamine (I), $[\alpha]_D^{20}$ +60°, and the corresponding alcohol (XV), $[\alpha]_D^{20}$ +18.9°, is undoubtedly due to the error (pointed out by Acharya and Brown[7]) in the assignment[1] of the configuration of this alcohol. Its configuration should be amended to (XVI).[7]



XV



XVI



XVII

The alcohol (XVII), $[\alpha]_D^{26} - 60.9^\circ$, was obtained by Acharya and Brown[7] by the reduction of (-)-*trans*-caran-2-one (VIII) with lithium aluminium hydride. In a parallel study[8] we find that (XVII) has $[\alpha]_D^{20} - 54^\circ$. These values are clearly in good agreement with those of our corresponding amine (II), $[\alpha]_D^{20} - 58.5^\circ$, and are compatible with the rotation, $[\alpha]_D^{20} + 60^\circ$, given by Kuczyński, *et.al*[1] for the amine (I), the enantiomorph of (II).

A more detailed account of the preparation of the amines (II-VII) which includes evidence for their probable conformations is now being prepared. Studies on their deamination are in progress.

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