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THE BOAT-CHAIR CONFORMATION OF
ENDO-1,5-DIMETHYLBICYCLO (3,3,1) NONAN-3-OL

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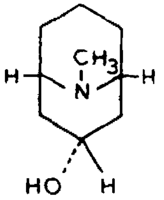
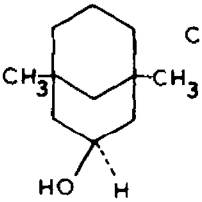
The recent determination (1) of the preferred conformation of 3-α-granatanol (I), a 9-aza-bicyclo (3,3,1) nonan-3-ol, prompts us to describe our findings in the analogous carbocyclic system.

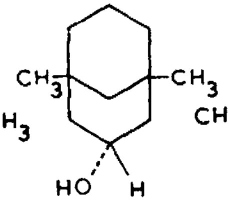
The epimeric 1,5-dimethylbicyclo (3,3,1) nonan-3-ols (II) and (III) have been prepared in the following manner. Hydroboration (2) of 1,5-dimethylbicyclo (3,3,1) non-2-ene (3) gave the exo-3-ol (II) accompanied by a small amount of the corresponding exo-2-ol. Jones oxidation of (II) gave the ketone (IV). Lithium aluminium hydride reduction of (IV) proceeded in a highly stereospecific manner giving the endo-3-ol (III) virtually uncontaminated by (II) as indicated by gas-liquid chromatographic analysis. The p.m.r. spectra of (II), (III) and (IV) exhibited sharp unsplit C-methyl (6H) signals at τ = 9.10, 9.06 and 9.01 respectively, thus confirming the symmetrical substitution pattern in all three compounds.



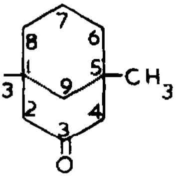
[I]



[II]

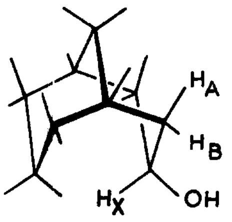


[III]

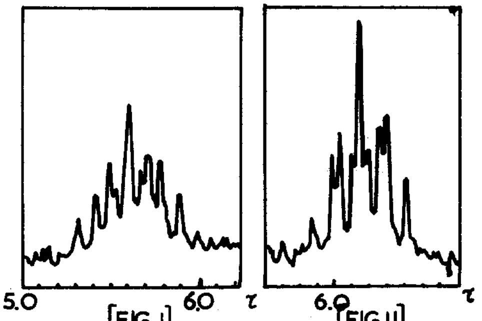


[IV]

The I.R. spectrum of (II) showed 'abnormal' methylene bands(3,4) at 1473 and 2990 cm.$^{-1}$ indicative of the twin-chair conformation (V) and the p.m.r. spectrum showed the carbinyl proton [the X part of an A_2B_2X system (5)] as a clear nine-line pattern (fig.1) centred at $\tau = 5.62$, ($J_{AX} = 11.4$ cps., $J_{BX} = 6.6$ cps.). The low-field position of this signal presumably is due to deshielding by the endo C_7 - hydrogen atom [cf. neoisopinocampheol (6), C$\underline{H}$OH, $\tau = 5.69$]. The epimeric alcohol (III) showed a weak band in the infra-red at 1473 cm.$^{-1}$ with no significant absorption at 2990 cm.$^{-1}$, and the carbinyl proton in the p.m.r. spectrum (fig.2) appeared again as a well-resolved nine-line pattern centred at $\tau = 6.15$ ($J_{AX} = 9.0$ cps., $J_{BX} = 6.6$ cps.).



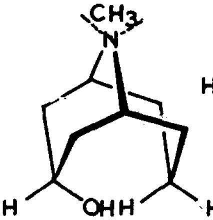
[V]



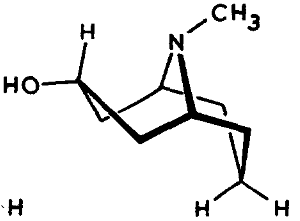
[FIG.I] [FIG.II]

60 MC. PMR SPECTRA IN CCl_4

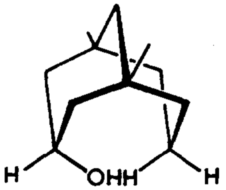
Chen and Le Fevre have reported 3-α-granatanol (I) to be an equilibrium mixture of two conformers (VI) and (VII) with the latter in preponderance (86%). It is difficult to envisage the conformer (VIII) as a major contributor to such an equilibrium in the carbocyclic system since even the presence of two $\underline{\text{endo}}$-hydrogen atoms on C_3 and C_7 in the established twin-chair conformation of 1,5-dimethylbicyclo (3,3,1) nonane (4) is known to produce lateral distortion of the two ends of the molecule. Accordingly we suggest that in the carbocyclic case such a conformational equilibrium would involve species (IX) and (X). In addition, the magnitude (7) of the observed coupling constants in (III) would suggest that the preferred conformation is (IX).



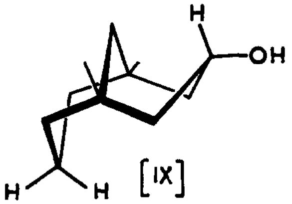
[VI]



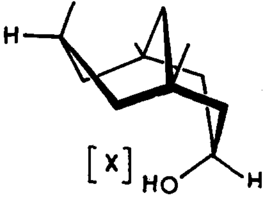
[VII]



[VIII]



[IX]



[X]

The Australian workers quote J_{AX} = 11 cps. and J_{BX} = 5 cps. for (VII) and $J_{AX} + J_{BX}$ = 5 cps. for (VI). Application of these values to (IX) and (X) respectively in an attempt to establish the position of this equilibrium (8) leads to a value of >100% of conformer (IX). Although a better value for J_{AX} in (IX) might be 13.5 cps. (9) leading to a figure of 86% of conformer (IX) in the endo-3-ol (III), at ambient temperatures, these approaches lack a rigorous evaluation of all the coupling constants involved in the particular A_2B_2X systems under discussion. Accordingly low temperature p.m.r. studies on (II) and (III) and the related bisnordimethyl compounds are now in hand.

ACKNOWLEDGEMENTS

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