

SYNTHESIS AND CONFORMATIONAL MOBILITY OF BICYCLO(3,3,3)UNDECANE (MANXANE¹)

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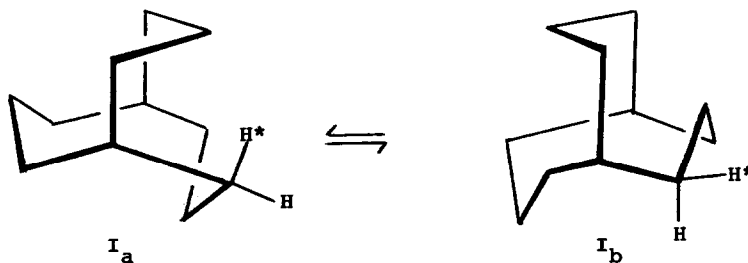
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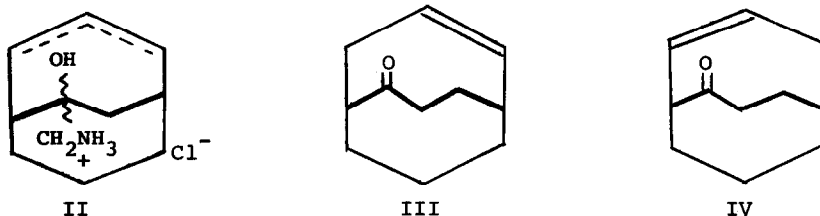
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In view of the current interest in propellane² chemistry and in order to extend our studies of the effects of transannular crowding in bridge-ring systems³ we turned our attention to the hitherto unknown bicyclo(3,3,3)undecane ring system⁴ in which there is the possibility of the degenerate conformational change ($I_a \rightleftharpoons I_b$).



An isomeric mixture of bicyclo(3,3,2)dec-2-ene-9 and 10-ones⁵ on treatment with HCN furnished a 2:3 mixture of the expected cyanohydrins and starting ketones which was acetylated to yield the corresponding mixture of cyanohydrin acetates and unreacted ketones. Lithium aluminium hydride reduction and treatment with HCl gas permitted the isolation of the hydroxyamine hydrochlorides (II) (mp 219-221^o), which on subsequent treatment with nitrous acid at 5^o yielded an isomeric mixture of two olefinic ketones in the ratio 1:1, separable by preparative thin layer chromatography. The more polar isomer was assigned the bicyclo(3,3,3)undec-2-en-9-one structure (III) on the basis of its n.m.r. spectrum, a multiplet at 4.2 τ (2H) and a complex multiplet at 7-8.8 τ (14H). The n.m.r. spectrum of the less polar ketone showed a multiplet at 4.2 τ (2H), complex multiplet at 6.8 τ (1H) and a complex envelope at 7-8.8 τ (13H) compatible with structure (IV).



Hydrogenation of the mixture of III and IV, produced a single ketone bicyclo(3,3,3)undecan-2-one mp 218-220°C (M^+ 166, $\nu_{\max}^{\text{CCl}_4}$ 1690 cm^{-1}) which easily incorporated three deuterium atoms on treatment with ca. 0.1 M Sodium deuterioxide/Dioxan. (M^+ 169).

Lithium aluminium hydride reduction of this ketone produced a single alcohol mp 205-210° which showed two intense doublet absorptions centred at 1040 and 970 cm^{-1} ⁵. Wolff Kishner reduction of the ketone yielded the hydrocarbon bicyclo(3,3,3)undecane as a highly volatile, crystalline solid. The symmetry (C_{3h}) of the molecule is reflected in the high melting point (191-193°) and the simple infrared spectrum[†]; only five bands being observed in the fingerprint region, with no high frequency methylene stretching or scissoring frequencies due to severe transannular methylene pair interactions being present⁶.

The 220 MHz ^1H spectrum of the hydrocarbon (measured at 35° in CDCl_3) corresponds to rapid (in the n.m.r. sense⁷) interconversion between conformations I_a and I_b and comprises an ill resolved multiplet ($W_{1/2}$ ca 17 Hz) centred at 7.63 τ (2H) from the bridgehead protons and a very tightly coupled multiplet (approximate range 8.45-8.55 τ) (18H) from the methylene protons. As can be seen from the Figure the process $I_a \rightleftharpoons I_b$ interchanges methylene protons between non-equivalent sites. At room temperature exchange is sufficiently rapid to cause collapse of the chemical shifts involved⁷. From a study of the temperature dependence of the ^1H spectrum[†] one may estimate using absolute rate theory (assuming a transmission coefficient of $\frac{1}{2}$) that the free energy of activation ΔG^* for the process $I_a \rightleftharpoons I_b$ is 11 \pm 2 kcal/mole at -60°.† In order to obtain accurate activation parameters for conformational processes involving the

manxane skeleton suitable derivatives are essential and synthetic work along these lines is in progress.

* This is to be compared with the very simple infrared spectrum of the symmetry related trishomobarrelene which has recently been synthesised⁸, only seven significant bands being observed⁹ in the fingerprint regions.

† Details of the variable temperature work (mainly at 100 MHz) will be given later, but it may be said here that the "frozen" Spectrum, corresponding to slow exchange between I_a and I_b, is observed at -80°C with CDCl₃/CD₂Cl₂ (1:1) as solvent. Raising the temperature from +35°C to +150°C (in hexachlorobutadiene) has no kinetically significant effect on the spectrum. Concordant 220 Mz ¹H results (spectra by courtesy of Dr. J.K. Becconsall, I.C.I. Ltd., Runcorn, Cheshire) were obtained in the range +35°C to -35°C in CDCl₃.

‡ This value may be compared with the free energy barrier of 15.7 kcal/mole obtained recently (H. Gilboa, J. Altman and A. Loewenstein, J. Amer. Chem. Soc. 91 6062, 1969) for the related 3,3 difluoro[4,4,4]propellane

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