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ALICYCLIC COMPOUNDS V

STUDIES RELATING TO THE SYNTHESIS OF CYCLODECADIENONE - FRAGMENTATION OF δ - KETO TOSYLATES

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The base catalysed fragmentation of the tosylate of the cis- hydroxy decalone (I) to the cyclodecadienone (III) has been described[1]. Between the two conformations (IV and VI) for this cis-decalone, the steroid conformation (IV) would appear to be favoured since after cancelling common 1,3-diaxial interactions there are left a CH_3/CH_2 interaction corresponding to 3.6 k.cal/mole in IV compared to a total of 4.2 k.cal/mole in the conformation VI, arising from CH_3/OH interaction of approximately 2.4 k.cal/mole, CH_3/H interaction of 0.9 k.cal/mole and a 3-alkyl ketone interaction of 0.9 k.cal/mole. In the steroid conformation IV the ideal antiperiplanar geometry of all centres for a concerted fragmentation[2] is present, the C_8-OH bond is antiperiplanar to the C_9-C_{10} bond which is antiperiplanar to the C_4-eq.H bond.

The epimeric hydroxy decalone (II) has now been obtained. Conformational analysis suggests that this epimer would exist in the non-steroid conformation VII. The total energy content for the steroid conformation V would amount to ca. 8.4 k.cal/mole against 2.7 k.cal/mole for the non-steroid conformation VII.

In the non-steroid conformation VII, the antiperiplanar geometry required for a concerted fragmentation is also present. The steric disposition of the C_8-OH bond, C_9-C_{10} bond and the C_4-eq.H bond in this conformation exactly corresponds to the disposition of these centres in the conformation IV of its epimer (I).

This led us to examine the action of $KOBu^t$ in hot Bu^tOH on the tosylate of the hydroxy decalone (II) in the expectation that it would suffer fragmentation to an isomer of the cyclodecadienone (III) where the non-conjugated double bond will be cis. Surprisingly the tosylate was quantitatively recovered unchanged under conditions in which the tosylate of its epimer (I) suffered ready fragmentation.

Though both epimers in their more stable conformation possess the requisite geometry for a concerted fragmentation, the above difference in reactivity between them can presumably be ascribed to the ease with which base can remove the C_4-eq.H to generate the anionic charge which triggers fragmentation. In the conformer IV of the β-epimer (I) the C_4-equatorial hydrogen is more exposed than the C_4-axial hydrogen which is shielded by the C_6-axial methyl group. Base can readily remove the equatorial hydrogen and the development of anionic charge at C_4 is synchronous with the concerted movement of electrons which result in fragmentation. In the conformer VII of the α-epimer (II) the requisite C_4-equatorial hydrogen is relatively less exposed, being shielded by the concave cage of the cis-decalin ring in consequence of which base cannot easily remove this hydrogen to generate the required anionic charge which would trigger concerted fragmentation. It thus appears that in addition to the steric requirement of antiperiplanar geometry, the accessibility to base of the hydrogen participating in the concerted process is also a determining factor.

Contrary to our previous report[1], $NaBH_4$ reduction of the 3-ethyleneketal of cis-6,6,9-trimethyl-decalin-3,8-dione has been found to be nonstereospecific giving after deketalisation a mixture of I and II which could be readily separated by repeated crystallisation. The β-isomer (I) had m.p. 140 , acetate m.p. 88 and tosylate m.p. 150 and the α-isomer (II) had m.p. 116, acetate m.p. 75 and tosylate m.p. 178. LAH reduction of 6,6,9-trimethyl-$\Delta^{4,10}$-octalin-3,8-dione also gave a mixture of diols; a crystalline diol m.p. 182 which on MnO_2 oxidation gave a crystalline hydroxyoctalone m.p. 125 which on catalytic reduction afforded the hydroxy decalone (I) m.p. 140 [1] and

an oily diol which on MnO_2 oxidation gave an oily hydroxy octalone which on catalytic reduction gave the hydroxy decalone (II) m.p. 116. $NaBH_4$ reduction of the octalindione was however more stereospecific giving the crystalline diol m.p. 182 in over 95% yield.

Fragmentation of the tosylate of the β-isomer (I) to the cyclodecadienone (III) has been described[1]. We have now obtained further support in favour of the structure (III) by Lemieux - von Rudloff[3] periodate-permanganate oxidation to laevulinic acid and $\beta\beta$-dimethyl glutaric acid which were identified by comparison with authentic samples by thin layer chromatography. The N.M.R. spectra of III had peaks at 9.04 τ (singlet), 8.85 τ (singlet) for the gem-dimethyl groups and at 8.15 τ (singlet) for the vinyl methyl group besides absorption between 4.7 - 3.95 τ for vinyl hydrogens.

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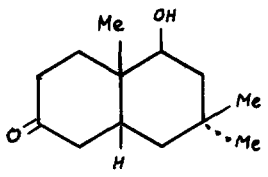

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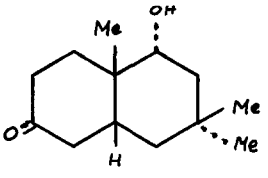

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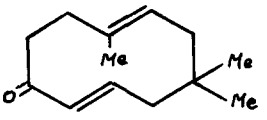

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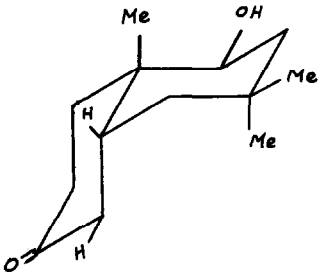

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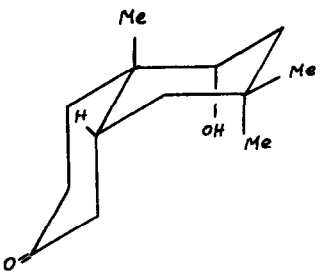

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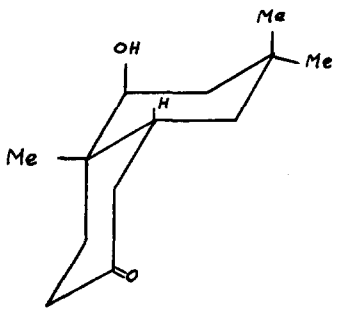

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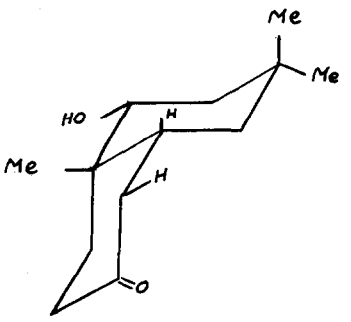

VII