Regiospecific *syn*-Elimination from the Acid-catalysed Reactions of 9-Hydroxy-10-methyldecahydronaphthalenes

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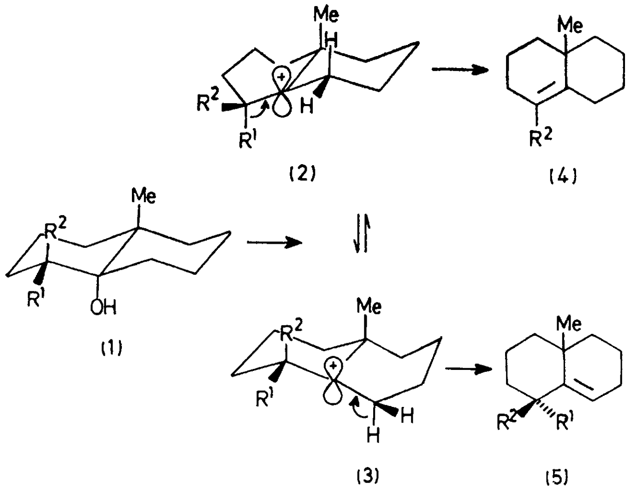
Summary The H_2SO_4–HOAc–Ac_2O catalysed dehydration of 9-hydroxy-10-methyl-*cis*- and *trans*-decahydronaphthalenes occurs regiospecifically without skeletal or methyl rearrangement and is interpreted in terms of the intermediacy of a tight ion pair where the departing oxy-anion acts as the base in the removal of a *syn*-proton.

REACTION of both 9-hydroxy-10-methyl-*trans*- and *cis*-decahydronaphthalene with H_2SO_4–HOAc–Ac_2O,[1] by analogy with kinetic[2] and related studies[3] of steroid C(5)-alcohols, would take place superficially at least, *via* the intermediacy of a common C(9)-carbonium ion. We report deuterium labelling experiments which, allow a measure to be made of the 'memory effect' in these reactions.

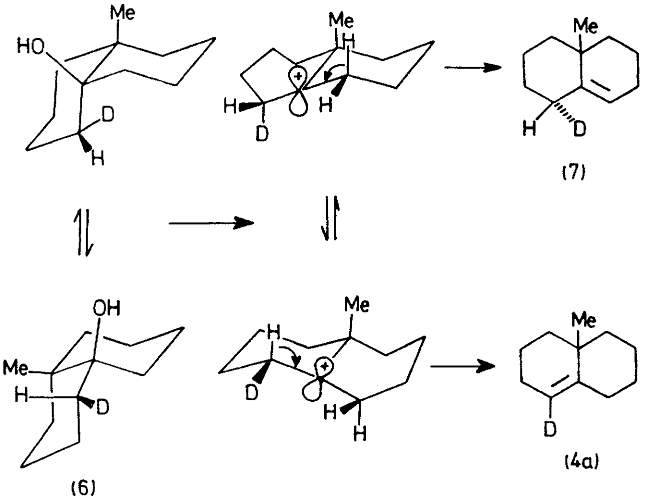
Reaction of *r*-1-deuterio,*t*-9-hydroxy-10-methyl-*trans*-decahydronaphthalene (**1a**) (0·4 M) with H_2SO_4 (0·025 M) and acetic anhydride (1·6 M) in acetic acid has been shown to give a 1 : 1 mixture of 1-deuterio-$\Delta^{1,9}$-10-methyl- and *r*-8-deuterio,$\Delta^{1,9}$-*c*-10-methyl-decahydronaphthalene (**4a**) and (**5a**). Similar reaction of *r*-1-deuterio,*t*-9-hydroxy-10-methyl-*cis*-decahydronaphthalene (**6**) afforded a 1 : 1 mixture of 1-deuterio-$\Delta^{1,9}$-10-methyl- and *r*-8-deuterio,-$\Delta^{1,9}$-*t*-10-methyl-decahydronaphthalene (**4a**) and (**7**). The mass spectrum of the olefin product mixtures showed that no measurable loss (<5%) of deuterium had occurred and integration of the vinyl proton signal in the ^1H n.m.r. spectra was equivalent to 0·5 H. In the single-frequency off-resonance decoupled ^{13}C n.m.r. spectra C(1) was a singlet at δ $119{\cdot}2_5$ p.p.m. superimposed on a triplet centred at δ $118{\cdot}9_8$ p.p.m. (J $1{\cdot}1_7$ p.p.m.) and C(8) a singlet at δ $32{\cdot}6_4$ p.p.m. superimposed on a triplet centred at δ $32{\cdot}3_6$ p.p.m. (J $0{\cdot}9_5$ p.p.m.). The peak heights of C(2) and C(7) were reduced by long-range coupling with deuterium. The intensities of the C(4) and C(5) signals with respect to the C(10)-CH_3 signal for both product mixtures were identical within the limits of accuracy and reproducibility ($\pm 5\%$) with those of an unlabelled sample of the olefin when the spectra were obtained under identical conditions. The failure to detect deuterium at C(4) and C(5) indicates that methyl migration and skeletal rearrangement involving spiran intermediates do not successfully compete with 1,2-elimination.



a; $R^1 = H$, $R^2 = D$
b; $R^1 = D$, $R^2 = H$

Scheme 1

Elimination from the alcohol (**1a**) to give the olefin (**4a**) occurs by loss of the C(1)H which is *syn* to the departing C(9)-group and therefore because of the symmetry of the substrate, the olefin (**5a**) must be formed by loss of *t*-C(8)H-(*r*-1-D) (Scheme 1). The C(9)-carbonium ion conformers (**2**) and (**3**) will be identical in energy and hence the equilibrium constant for their interconversion will be unity. If the rate of interconversion between these conformers were slow relative to the rate of proton loss then from the epimeric 1-deuterio-alcohol (**1b**), the olefins (**4b**) and (**5b**) would be formed in equal amounts. The alcohol (**1b**), however, on reaction with H_2SO_4–Ac_2O–HOAc affords a $2{\cdot}2(\pm 0{\cdot}4):1$ mixture of the olefins (**5b**) and (**4b**), which demonstrates that the rate of interconversion between the carbonium ion conformers (**2**) and (**3**) (Scheme 1) is at least comparable with the rate of proton loss.



Scheme 2

In contrast with the reactions of the alcohols (**1a**) and (**1b**) where a proton (deuteron) *anti* to the C(10)-methyl group is lost, the alcohol (**6**) (Scheme 2) gives the olefins (**4a**) and (**7**) by stereospecific loss of C(1)H and *t*-C(8)H(*r*-1-D) respectively, both protons *syn* to the C(10)-methyl and leaving C(9) group.

The regiospecific loss of hydrogen (deuterium) from these alcohols in each case *syn* to the C(9)–O group demonstrates that transfer of an oxy-anion to the opposite face of the intermediate C(9)-carbonium ion species does not compete with product formation. For each substrate the departing oxy-anion, presumably held as a tight ion pair, is thought to act as the base in the removal of a *syn* proton (deuteron).

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