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A PROBE OF THE RELATIVE RATE OF INTERCONVERSION OF CARBONIUM ION CONFORMERS *vs* PROTON LOSS IN 9-HYDROXY-10-METHYLDECAHYDRONAPHTHALENES

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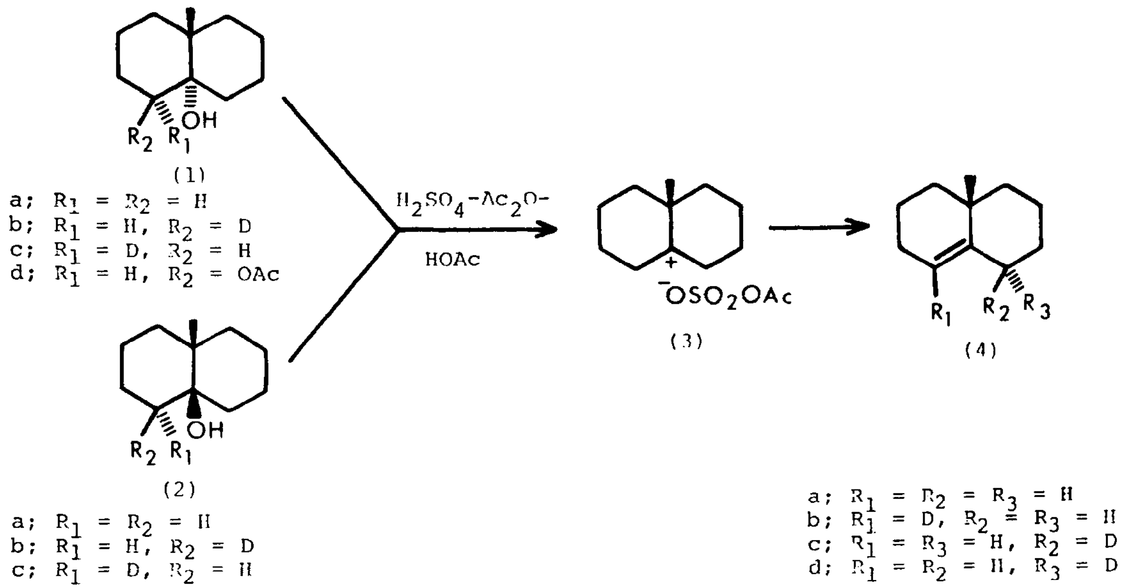
Abstract: Deutero-alcohol (2b) was prepared and dehydrated with H_2SO_4-Ac_2O-HOAc to give a kinetic isotope effect demonstrating anion mobility within the intermediate carbocation-anion ion pair.

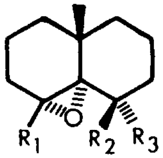
Reaction of 9-hydroxy-10-methyl-*trans*- and *cis*-decahydronaphthalene (1a) and (2a) with H_2SO_4-Ac_2O-HOAc takes place, superficially at least, via the intermediacy of a common C(9)-carbonium ion (3) (Scheme 1).[1] The loss of hydrogen (deuterium) from alcohols (1a) and (2a) to form olefin (4) is stereospecific with loss of a proton *syn* to the C(9)-O[2]. For each substrate the departing oxyanion[3], $^-OSO_2OAc$, presumably held as a tight ion pair, is thought to act as base in the removal of a *syn*-axial proton. Transfer of the oxyanion to the opposite face of



Scheme 1

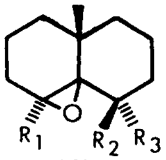
the intermediate carbocation does not compete with proton loss from the cation[4].

We have now prepared the deutero-alcohol (2b) in order to determine the magnitude of the kinetic isotope effect for proton (deuterium) loss from this alcohol on reaction with H_2SO_4-Ac_2O-HOAc as a probe of the internal mobility of the intermediate carbocation-anion pair. Reaction of olefin (4a) with meta-chloroperbenzoic acid gave an inseparable mixture of epoxides[2] (5a) and (6a)



(5)

a; $R_1 = R_2 = R_3 = H$
b; $R_1 = D$, $R_2 = R_3 = H$
c; $R_1 = R_3 = H$, $R_2 = D$

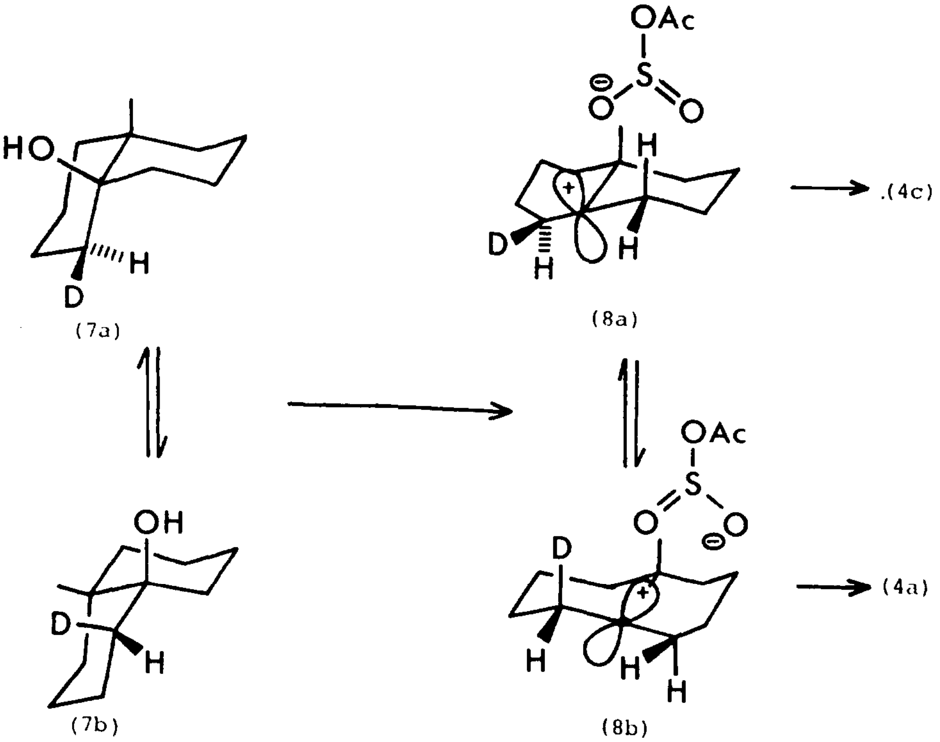


(6)

a; $R_1 = R_2 = R_3 = H$
b; $R_1 = D$, $R_2 = R_3 = H$
c; $R_1 = R_3 = H$, $R_2 = D$

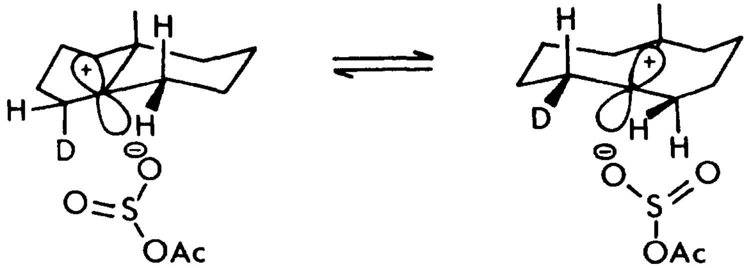
which on reaction with LAD[4,5] gave alcohols (1b) and (1c) [(43 : 57; 95% from olefin(4a)] which were separated by column chromatography. Reaction of the former alcohol (1b) with H_2SO_4-Ac_2O-HOAc gave a (1 : 1 ; 80%) mixture of deutero-olefins (4b) and (4c) by syn loss of water[1] and this alkene mixture was epoxidised with meta-chloroperbenzoic acid. The resulting epoxides (5b), (6b), (5c) and (6c) were reduced with LAH to give alcohols (2b), (1b) and (1c), the former being separable from (1b) and (1c).

Reaction of alcohol (2b), which exists as a rapidly exchanging mixture of chair-chair conformers[6] (7a $\rightleftharpoons$ 7b ; $\Delta H^{\ddagger}$ 66.7 ± 1.3 kJ mol^{-1}), with H_2SO_4-Ac_2O-HOAc gave olefin (4) (65-70%) (Scheme II). The ^{13}C n.m.r. spectrum[7] showed the C4 and C5 signals were not reduced in height compared with the carbons of an authentic undeuterated sample of (4a) thereby excluding methyl migration and spiran intermediacy in the formation of the olefin. C1 appeared as a singlet centred at 32.6 p.p.m. (4a) superimposed on a triplet centred at 32.4 p.p.m. (4c). Analysis by gc/ms of the olefin and in particular the intensity of the peaks at m/e 152, 151 and 150 in comparison with the peaks at 151, 150 and 149 of an authentic unlabelled sample of olefin indicated the olefins (4a) and (4c) to be in the ratio 1 : 2.2. These data are consistent with 1,2-syn-elimination occurring with a kinetic isotope effect k_H/k_D = 2.2 ± 0.2 which demonstrates that for the dehydration of alcohol (2b) the rate of interconversion between the carbonium ion - anion tight ion pair conformers (8a) and (8b) is at least comparable with the rate of proton loss. The isotope effect is comparable to

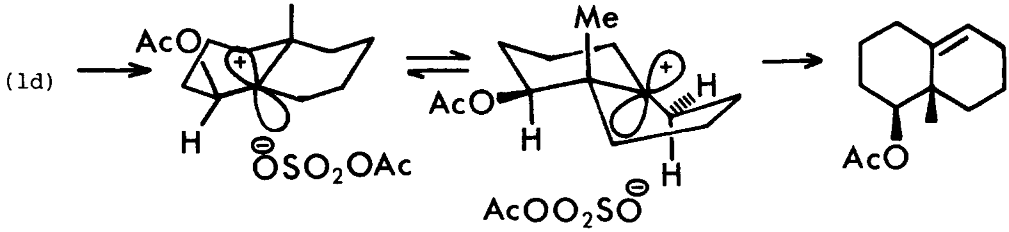


Scheme II

that observed for 1,2-syn proton loss from deutero-alcohol (1c) (k_H/k_D = 2.2 ± 0.4). These two reactions proceed via the intermediacy of a carbocation^{2,3} which differs only in the face of the carbocation to which the departing oxyanion is held in a tight ion pair configuration. The angular methyl group for the β-face ion pair (8) would be expected to reduce the mobility of the anion in the ion pair compared with the less hindered ion pair (9). The comparability of the kinetic isotope effects for these two systems indicates that the angular methyl does not reduce mobility of (8a ⇄ 8b) sufficiently for its effect to be felt on proton (deuterium) loss. In the limit if this interconversion were slow compared with proton loss no primary kinetic isotope effect would be observed.



(9)



(11) (12) (10)

Scheme III

The mobility of the ion pair complex (8) further supports the suggestion[8] (Scheme III) that the stereospecific proton loss observed in formation of olefin (10) from alcohol (1d) results from the intermediacy of a carbocation - oxyanion ion pair complex where the anion has sufficient mobility within the complex where a 1,2-methyl migration ($11 \rightleftharpoons 12$) is occurring for it to act as base in the removal of the proton.

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