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AN INVESTIGATION OF THE CONFORMATIONAL DYNAMICS OF ION-PAIR INTERMEDIATES IN THE *SYN*-ELIMINATION OF 8a-METHYLDECAHYDRONAPHTHALEN-4a-OLS†

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Abstract—The (4aβ,8aβ)-8a-methyl(5βD)decahydronaphthalen-4a-ol has been prepared and its reaction with H_2SO_4–Ac_2O–HOAc shown to occur with a k_H/k_D of 2.2 ($\pm$0.2) by loss of a proton (deuteron) *syn* to the departing oxy-anion. The results are used as a probe of carbocation-anion conformational mobility.

THE unsuccessful attempt by Westphalen[1] to acetylate the tertiary alcohol of 3β,6β-diacetoxy-5α-cholestan-5-ol (**1**) with H_2SO_4–Ac_2O–HOAc prompted interest, firstly in the structure[2] of the major rearranged product 5-methyl-19-nor-5β-cholest-9(10)-ene-3,6-diol diacetate (**2**) and secondly in the mode of action of the reagents[3] (Scheme 1). We have more recently studied the reaction of several 8a-methyldecahydronaphthalene-4a-ols with H_2SO_4–Ac_2O HOAc in an attempt to probe the detailed mechanism of reaction. In the absence of ring substituents 8a-methyl-*trans*- and *cis*-decahydronaphthalene-4a-ol (**3a**) and **4a** give 8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene (**5a**) in reactions which do not involve skeletal reorganisation, Me migration or spiran intermediacy. The product **5a** from both alcohols results from 1,2-elimination in reactions believed to involve the intermediacy of 8a-methyldecahydronaphthalen-4a-yl cation (**6**) formed by heterolysis of an initially produced intermediate acetyl sulphate intermediate.[4]

Reaction of deutero-alcohol **4b**, which exists as a dynamically equilibrating mixture of the two chair–chair conformers[5] (Scheme 2) with H_2SO_4–Ac_2O HOAc gives an equal mixture[4] of the deutero-alkenes (**5b** and **5c**). The cation intermediate produced from alcohol **4b** superficially is identical to the cation produced from similar heterolysis of the C–O bond of the epimeric alcohol **3b** (Scheme 3), however the latter reaction does not give an equal mixture of **5b** and **5c**, instead giving a mixture (1:2.2) of **5a** and **5c**.

Failure to observe loss of D from the reaction of alcohol **4b** suggests either that proton loss in the formation of alkene **5b** and hence **5c** is stereospecific and *syn* or alternatively that a large kinetic isotope effect favours loss of a proton.

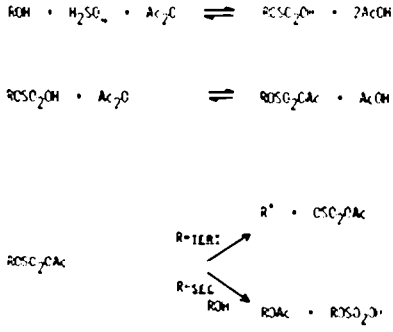
We now report the synthesis of alcohol **4c** and a study of its dehydration reaction with H_2SO_4–Ac_2O HOAc to measure the kinetic isotope effect and probe cation–anion mobility, information presently inaccessible by other methods of investigation.[6]

RESULTS AND DISCUSSION

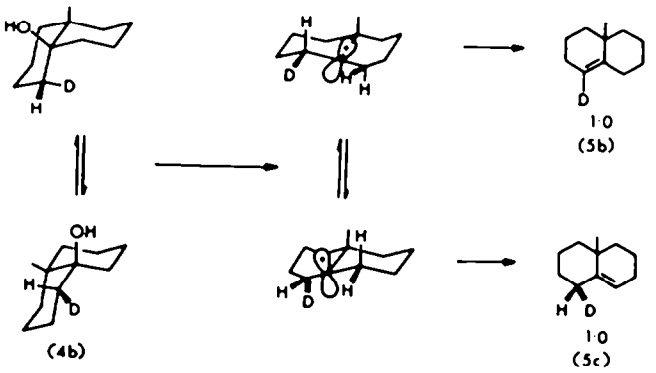
The synthesis of alcohol **4c** was affected in the following manner (Scheme 4). The epimeric 4,4a-epoxy-8a-methyl-*trans*- and *cis*-decahydronaphthalenes (**7a**), to date unseparated, were reacted with LAD to produce alcohols **3c** and **4b** which are readily separable. The former alcohol **3c** was dehydrated using H_2SO_4–Ac_2O–HOAc. This reaction is known to occur by *syn*-elimination[4] and the reaction is amenable to scaling up. The mixture of deuterated alkenes **5b** and **5d** was reacted with *m*-chloroperbenzoic acid and the deuterated epoxide mixture (**7b–e**) so produced reacted with LAH[7] to give three deuterated alcohols **3b**, **3c** and **4c**. The labelled *trans*-8a-methyldecahydronaphthalen-4a-ols (**3b** and **3c**) were separated by chromatography from the required stereospecifically labelled *cis*-8a-methyldecahydronaphthalene-4a-ol (**4c**).

Reaction of this latter alcohol **4c** with H_2SO_4 Ac_2O–HOAc gave a 1:2.2 ($\pm$0.2) mixture of alkenes **5a** and **5d** (Scheme 5). The signals due to C1 and C8 were not reduced in height in the ^{13}C NMR spectrum compared with the signals of an authentic sample of alkene **5a**, confirming that Me migration and/or spiran intermediacy do not compete with loss of a proton adjacent to the departing oxy-anion. The signal for C1 was a singlet, 32.6 ppm, superimposed on a triplet centred at 32.4 ppm and the olefinic signal in the ^1H NMR spectra integrated as one proton. The ratio of alkenes **5a** and **5d** was determined from the gc/ms of the mixture from, in particular, the intensity

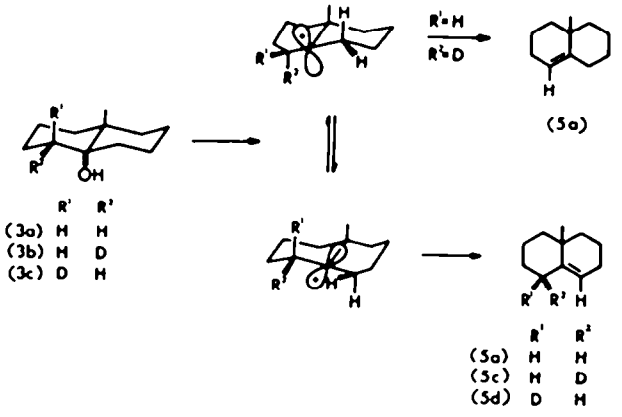
†For a preliminary report of this work see J. M. Coxon, G. W. Simpson, and J. A. Ussher, *Tetrahedron Letters* 3631 (1982).



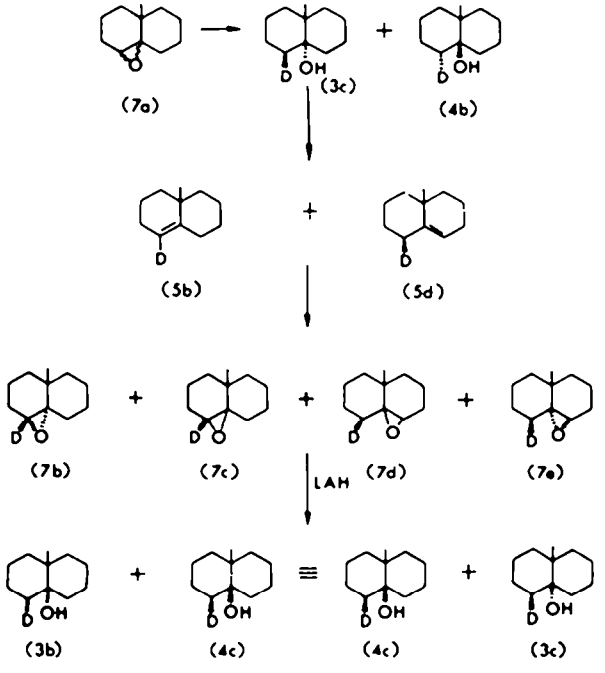
Scheme 1.



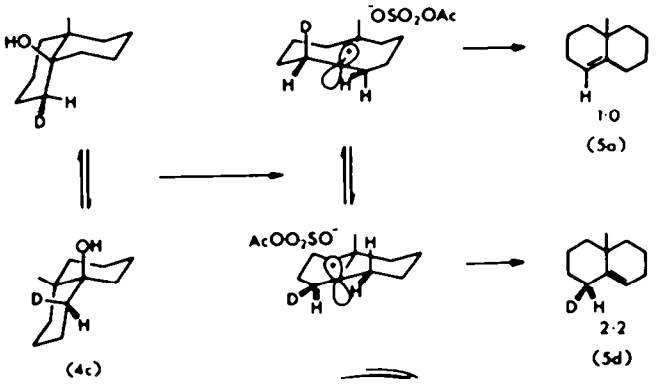
Scheme 2.



Scheme 3.



Scheme 4.



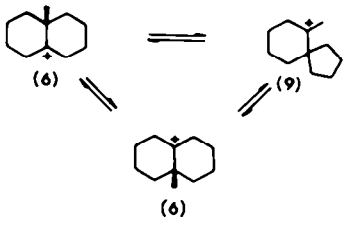
Scheme 5.

of the peaks at m/z 152, 151 and 150 in comparison with the peaks at 151, 150 and 149 of an authentic unlabelled sample of the olefin **5a**. The carbocation intermediate formed by C–O bond heterolysis in alcohols **4c** and **4b** (Schemes 5 and 2) can exist in two extremes of chair-boat conformation. From these two conformations it can be seen that each of the protons or deuteron adjacent to the carbocation centres can in one or other of the conformations present an appropriate orientation in the plane of the carbocation p-orbital to facilitate proton (deuteron) loss and alkene formation. The presence of a kinetic isotope effect (k_H/k_D 2.2 ± 0.2) in the reaction of alochol **4c** and its magnitude demonstrate firstly that the stereospecificity observed in the formation of alkene **5b** from alcohol **4b** does not result from a large kinetic preference for proton *vs* deuteron loss. Secondly the result shows a stereochemical preference in the loss of a proton adjacent to the departing oxy-anion. Furthermore the presence of a measurable kinetic isotope effect indicates that mobility of the carbocation conformers is at least comparable with the rate of proton loss since if this were not the case and interconversion of the carbocation conformers was slow, no kinetic isotope effect would be observed because the starting alcohol gives equal mixtures of the carbocation in the two extremes of conformation.

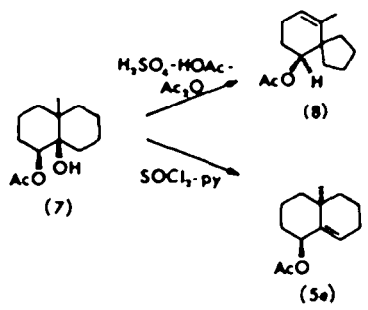
The rate of conformational change of carbocations in cyclic systems has not proved particularly amenable to study and has been a matter of some debate.[8] Whalen has recently argued[9] that the stereochemistry of diol formation from naphthalene tetrahydro epoxides is related to the rate of change of conformation of the intermediate benzyl cations. For acyclic carbocations simple conformational changes have been shown to be competitive with 1,2-hydride shifts[10] and similar results have recently been obtained for the spontaneous transformation of a naphthalene tetrahydroepoxide to ketone product.[9]

If the conformers of the carbocation formed from alcohol **4c** did not interconvert at a rate comparable to proton (deuteron) loss any kinetic preference for proton vs deuteron loss would be masked. The absence of deuteron loss from alcohol **4b** along with the measured kinetic isotope effect in the reaction of alcohol **4c** demonstrates unambiguously that for alcohols **4b** and **4c** the proton or deuteron CHD *syn* to the departing oxy-anion is lost. Because of the inherent symmetry of the deuterated *cis*-8a-methyldecahydronaphthalen-4a-ols (**4b** and **4c**) the loss of the proton from the adjacent CH_2 must also result from the β-face *syn* to the departing oxy-anion. Contrasting with this *syn*-elimination reaction of alcohol **4c** with H_2SO_4–Ac_2O–HOAc reaction of the alcohol with thionyl chloride gave a 1:1 mixture of alkenes **5b** and **5d** demonstrating that under these conditions the proton *anti* to the departing oxy group is lost.[4] The isotope effect observed for reaction of alcohol **4c** with H_2SO_4–Ac_2O–HOAc (k_H/k_D 2.2 ± 0.2) is comparable with that determined for similar reaction of alcohol **3b** (k_H/k_D 2.2 ± 0.4). These two reactions proceed via carbocation intermediates which differ in the face of the carbocation to which the oxy-anion is held as a tight ion pair. The angular Me group for the β-face ion pair might be expected to reduce the mobility of the complex compared with the α-face anion-carbocation ion pair. The comparability in isotope effects for these two reactions where the mobility of the intermediate carbocation-anion complex should differ somewhat suggests that the measured effect is a true kinetic isotope effect, and not a consequence of a comparatively slow rate of carbocation-anion conformer interchange.

The D labelled experiments[4] on 8a-methyl-*trans*- and *cis*-decahydronaphthalen-4a-ol (**3a** and **4a**) exclude Me migration and spiran intermediacy (Scheme 6) in the reaction with H_2SO_4· HOAc Ac_2O, conditions of reaction where carbocation intermediates are proposed. Reaction of (4aα,5α,8aα)-5-acetoxy-8a-methyldecahydronaphthalene-4a-ol (7) under these conditions gives 10-methylspiro[4,5]dec-9-en-6-yl acetate (**8**)[11] indicating that with an acetate adjacent and *syn* to the departing oxy-anion rearrangement to spiran can be induced. We have postulated[11] a similar rearrangement to account for the formation of *trans*-4a-methyl-1,2,3,4,4a,5,6,7-octahydronaphthalen-1-yl acetate (**5e**) from reaction of (4aα,5α,8aα)-5-acetoxy-8a-methyldecahydronaphthalen-4a-ol (7) with thionyl chloride in pyridine.



Scheme 6.



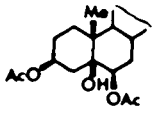
For substituted acetoxy-8a-methyldecahydronaphthalen-4a-ols the involvement of spiro carbocations in reaction with H_2SO_4–HOAc–Ac_2O is masked by isomerisation of the allylic acetate products. Reaction of (4aα,5β,8aα)-5-chloro-8a-methyldecahydronaphthalen-4a-ol (**4d**) with H_2SO_4–HOAc–Ac_2O results in formation of both *cis*- and *trans*-4a-methyl-1,2,3,4,4a,5,6,7-octahydronaphthalen-1-yl chorides (**5f** and **5g**).[12] The isomerisation of the chloride **5g** *via* an allylic cation under these conditions is unlikely to compete with substitution by acetate and the formation of the *cis*- isomer can be regarded as indicative of spiran intermediacy.

To probe the equilibrium of cations **6** and **9** 6-methylspiro[4,5]decan-6-ol (**10**)[13] was reacted with H_2SO_4–HOAc–Ac_2O and with $SOCl_2$–pyridine. Under the acidic conditions 8a-methyl-1,2,3,5,6,7,8,8a-octahydronaphthalene (**5a**) is formed demonstrating that in the absence of substituents the spiro cation **9** rearranges to cation **6**. The reverse of this rearrangement namely cation **6** to cation **9** does not occur as evidenced by the nonscrambling of D in reactions of the deuterated alcohols (**3b**, **3c**, **4b** and **4c**). With thionyl chloride–pyridine a mixture (7:3) of 6-methylspiro[4,5]dec-6-ene (**11**) and 6-methylenespiro[4,5]dec-6,(11)-ene (**12**) was obtained demonstrating that rearrangement of the chlorosulfate ester and formation of 8a-methyl-1,2,3,5,6,7,8,8a-octahydronaphthalene (**5a**) is not competitive with adjacent proton loss. These alkenes on standing in deuterochloroform slowly rearrange to alkene **5a**.

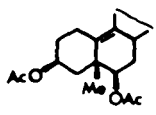
The decahydronaphthalen-4a-ol system and in particular deutero-8a-methyldecahydronaphthalen-4a-ols (**4c** and **4b**) provide a unique probe for understanding carbocation–ion pair conformation and the stereospecificity of the reactions with H_2SO_4–Ac_2O–HOAc studied to date suggest that this media may provide a general method of effecting *syn*-elimination. The method is mild and the rate of reaction is dependent on the concentration of sulfuric acid–acetic acid used and this therefore offers control in the reaction. *Syn*-elimination in tertiary alcohols to form alkenes typically involves further derivation[14] and the use of heat in the elimination step. The synthetic utility of the reagent is under investigation.

EXPERIMENTAL

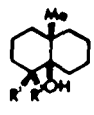
IR spectra were recorded on a Shimadzu IR27G spectrophotometer and ^{1}H NMR spectra on a Varian T60 spectrometer for $CDCl_3$ solns with $CHCl_3$ and Me_4Si as internal standards. ^{13}C NMR spectra were recorded on a Varian CFT20 spectrometer for $CDCl_3$ solns with Me_4Si as internal standard. Mass spectra were recorded on an A.E.I. MS902 spectrometer and gc/ms on a Hewlett Packard 5980A. Alumina used for chromatography was Spence grade H, deactivated by the addition of 10% v/v of 10% AcOH, and for dry column chromatography I.C.N. Pharmaceuticals alumina (Brockmann activity III/20) was used.



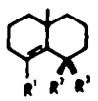
(1)



(2)

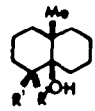


	R'	R'
(3a)	H	H
(3b)	H	D
(3c)	D	H

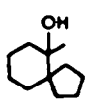


	R'	R'	R'
(5a)	H	H	H
(5b)	D	H	H
(5c)	H	H	D
(5d)	H	D	H
(5e)	H	H	OAc
(5f)	H	Cl	H
(5g)	H	H	Cl

(6)



	R'	R'
(4a)	H	H
(4b)	H	D
(4c)	D	H
(4d)	H	Cl



(10)

(11)

(12)

8a-*Methyl*-1,2,3,4,6,7,8,8a-*octahydronaphthalene* (**5a**)

Compound **5a** was prepared from 4a-methyl-1,2,3,4, 4a,5,6,7-octahydronaphth-7-yl acetate by known procedures[15] b.p. 90–95° at 25 mm (*lit.*[15] b.p. 86–88° at 26 mm), ν_{max}(film) 1665, 1003, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ_H 1.05, Me; 5.25, Wh/2 7 Hz, H5. ^{13}C NMR δ_C 19.1, C7; 22.5, C2; 24.3, Me; 29.3, C3; 32.6, C4; 34.8, C8a; 40.1, C8; 42.2, C1; 119.3, C5; 143.4, C4a. *m/z* 151 (12%), 150 (100), 149 (2), 136 (13), 135 (100), 134 (1).

Synthesis of (4aβ,8aβ)-8a-*methyl*(5βD)*decahydronaphthalen*-4a-*ol* (**4c**)

To a stirred soln of *m*-chloroperbenzoic acid (22 g) in dry ether (170 ml) was added **5a** (10 g) in dry ether (200 ml). After 5 hr excess $NaHCO_3$ was added and the mixture filtered through alumina (300 g). After removal of solvent a mixture (*c.* 5:7) of *cis*-, and *trans*-**7a** was obtained as a colourless oil (9 g) (M$^+$ 166.1327 $C_{11}H_{18}O$ requires: M$^+$ 166.1358) ν_{max}(film) 925, 895, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ_H 1.06, Me, *cis*-epoxide; 1.12, Me, *trans*-epoxide; 2.78, Wh/2 5 Hz, H1. ^{13}C NMR δ_C 15.6, Me, *trans*-epoxide, 16.4, Me, *cis*-epoxide; 20.6, 21.6, 21.6, 22.4, 23.1, 23.8, 24.4, 26.0, 30.2; 31.9, *cis*-C8a; 33.1, *trans*-C8a; 33.4, 34.1, 34.9, 35.8, 37.6; 60.2, *trans*-C4; 61.4, *cis*-C4; 64.1, *cis*-C4a; 65.3, *trans* C4a. *m/z* 167 (2.2%), 166 (39.2), 165 (3.7), 151 (12.9), 122 (27.5), 112 (100), 95 (38), 81 (54.8).

The mixture of epoxides **7a** (2g) was dissolved in tetrahydrofuran (20 ml) and lithium aluminium deuteride (0.5 g) added. The mixture was heated under reflux and stirred for 24 hr, cooled and sat Na_2SO_4aq carefully added. The mixture was filtered, the solvent removed from the filtrate and the residue adsorbed onto alumina (200 g). Elution with pentane gave **3c** (1.1 g). ν_{max}(film) 3500 cm^{-1}; ^1H NMR ($CDCl_3$) δ_H 1.02, Me. ^{13}C NMR δ_C 72.8, C4a; 35.0, C1, C8; 34.3, C5; 34.0, t, J 19 Hz, C4; 21.0, C2, C4; 20.8, Me; 20.3, C3, C6. Further elution gave mixed alcohol fractions (200 mg) followed by **4b** (700 mg) (M$^+$ 169.1563. $C_{11}H_{19}OD$ requires: M$^+$ 169.1596). ^1H NMR ($CDCl_3$) δ_H 0.97, Me. δ_C 35.9, C1, C8; 23.5, C2, C7; 22.2, C3, C6; 36.1, C4, C5; 73.4, C4a; 38.1, C8a; 23.0, Me. *m/z* 170 (4.2%), 169 (19.5), 154 (2.2), 113 (56), 112 (100), 111 (25.2).

To a stirred soln of **3c** (640 mg) in AcOH (20 ml) and Ac_2O (6 ml) was added rapidly a soln of H_2SO_4 in AcOH (6.2 ml, 1% v/v). After 60 s the mixture was poured into pentane (200 ml) and sat $NaHCO_3$aq (200 ml). Solid $NaHCO_3$ was added with vigorous stirring until effervescence ceased. The pentane extract was washed with sat $NaHCO_3$aq and water and dried with $MgSO_4$ and the solvent removed to give a mixture (1:1) of the alkenes, **5b** and **5d** (460 mg), ν_{max}(film) 1665, 1603, 985 cm^{-1}. ^1H NMR ($CDCl_3$) δ_H 1.05 (Me), 5.25, ($\frac{1}{2}$H) Wh/2 5 Hz, H5. ^{13}C NMR δ_C 19.1, C7; 22.5, C2; 24.3, Me; 28.3, C3; 32.4, 32.6, t, J 20 Hz, C4; 34.8, C8a; 40.1, C8; 42.2, C1; 119.3, 119.0, t, J 20 Hz, C5; 143.4, C4a; *m/z* 152 (12.1%), 151 (100), 150 (51.7), 137 (10.8), 136 (100), 135 (50).

The sample was homogeneous by gc and had an identical retention time with an authentic sample of **5a**.

The alkene mixture **5b** and **5d** (450 mg) was dissolved in ether (20 ml), and *m*-chloroperbenzoic acid (600 mg) added. The soln was allowed to stand overnight and washed successively with $NaHSO_3$aq, $NaHCO_3$aq and water; dried with $MgSO_4$ and the solvent removed to give a mixture of epoxides **7b–e** (380 mg), ν_{max}(film) 925, 895, 838 cm^{-1}. ^1H NMR ($CDCl_3$) δ_H 1.06, Me, *cis*-epoxide; 1.12, Me, *trans*-epoxide; 2.78, (0.5H), Wh/2 6 Hz, H1; ^{13}C NMR ($CDCl_3$) δ_C 15.62, 16.34, 20.59, 21.61, 22.45, 23.13*, 23.78, 24.45, 25.92, 26.01*, 30.22*, 31.93, 33.15, 34.08, 34.86*, 35.78*, 37.64, 60.29, 61.41*, 64.15*, 65.32 (peaks marked * are those which are substantially reduced in height compared to the ^{13}C NMR spectrum of the mixture of non-deuterated epoxides **7a**). *m/z* 168 (14.4%), 167 (100), 166 (6.8), 152 (33.4), 151 (46.1), 150 (7.9), 136 (43.7), 123 (46.1).

The mixture of epoxides **7b–e** (380 mg) was added to a suspension of LAH (0.5 g) in ether (25 ml) and the mixture stirred and heated under reflux for 2 hr. The mixture was cooled and quenched with sat Na_2SO_4aq. The mixture was filtered and the filtrate was dried with $MgSO_4$ and the solvent removed to give a mixture of the alcohols, **3b**, **4c**, and **3c** (330 mg) ^1H NMR ($CDCl_3$) δ_H 1.02, 0.97. Repeated chromatography on alumina, with ether–pentane (1:50) gave the more polar alcohol **4c**, (63 mg) (M$^+$ 169.1497 $C_{11}H_{19}DO$ requires: M$^+$ 169.1577). ^1H NMR ($CDCl_3$) δ_H 0.97, Me. ^{13}C NMR ($CDCl_3$) δ_C 35.9, C1, C8; 23.5, C2, C7; 22.2, C3, C6; 36.5, C4, C5; 73.4, C4a; 38.1, C8a; 23.0, Me. *m/z* 170 (13%), 169 (100), 168 (1), 154 (25).

Reactions of (4aβ,8aβ)-8a-*methyl*(5βD)*decahydronaphthalen*-4a-*ol* (**4c**)

(i) *With* H_2SO_4–Ac_2O–HOAc. The alcohol **4c** (30 mg) was dissolved in a mixture of AcOH (1.5 ml) and Ac_2O (0.3 ml). To this was added a soln of H_2SO_4 in AcOH (0.3 ml; 1% v/v). After 2 min, the mixture was poured into pentane (30 ml) and sat $NaHCO_3$aq (30 ml). Solid $NaHCO_3$ was added until effervescence ceased. The pentane extract was washed with sat $NaHCO_3$aq (30 ml) and water (30 ml), dried with $MgSO_4$ and the solvent removed to give a mixture of **5a** and **5d** (20 mg) (1:2.2 (±0.2)) identical (gc) with an authentic sample of alkene **5a**. ^1H NMR ($CDCl_3$) δ_H 1.05, (3H), Me; 5.25, (0.6H) H5; ^{13}C NMR ($CDCl_3$) δ_C 19.1, C7; 22.5, C2; 24.3, Me; 28.3, C3; 32.6, 32.4, t, J 19 Hz, C4; 26.0, C6; 34.8, C8a; 40.1, C8; 42.2, C1; 119.0, t, J 19 Hz, 119.3 C5; 143.4, C4a. *m/z* 150 (40%), 151 (100%), 152 (11), 137 (11), 136 (100), 135 (43).

(ii) *With thionyl chloride*. The alcohol **4c** (30 mg) was dissolved in pyridine (2 ml) and the soln cooled to freezing point in a dry ice–MeOH bath. $SOCl_2$ (2 drops) was added and the mixture allowed to warm then refrozen. This procedure was repeated several times until mixing was complete. The mixture was poured into water (10 ml) and ether (25 ml) and the ether layer separated and washed with dil H_2SO_4 and water and dried with $MgSO_4$. Removal of the solvent afforded a mixture (18 mg) of starting **8a** (*c.* 33%) and a (1:1) mixture the alkenes **4b** and **5d**. Gcms showed for the alkene mixture *m/z* 152 (7%), 151 (27), 137 (9), 136 (100), 135 (2).

Reactions of 6-*methylspiro*[4,5]*decan*-6-*ol* (**10**)

(i) *With* H_2SO_4–Ac_2O–HOAc. To a stirred soln of **10**[13] (50 mg) in AcOH (2.2 ml) and Ac_2O (0.26 ml) was added a soln of H_2SO_4 in AcOH (0.15 ml; 1% v/v). After 1 min, ether (15 ml) and sat $NaHCO_3$aq (15 ml) was added. $NaHCO_3$ was added until effervescence ceased. The ether extract was washed with sat $NaHCO_3$ (20 ml), dried with $MgSO_4$ and the solvent removed to give an oil shown by ^1H NMR and ^{13}C NMR to contain **5a** (38 mg) identical to an authentic sample. ^1H NMR ($CDCl_3$) δ_H 1.07, Me; 5.27, Wh/2 7 Hz, H5. ^{13}C NMR ($CDCl_3$) δ_C 19.1, 22.5, 24.4, 26.0, 28.6, 32.7, 34.8, 40.1, 42.3, 119.3, 143.9.

(ii) *With thionyl chloride*. To a soln of **10** (50 mg) in dry benzene (2.5 ml) and dry pyridine (0.3 ml) was added $SOCl_2$ (0.15 ml). After 2 hr ether (10 ml) was added and the mixture poured into a sat $NaHCO_3$aq (20 ml). The ether layer was separated and washed with dil H_2SO_4 and dried with $MgSO_4$. Removal of solvent afforded a mixture (7:3) of **11** ^1H NMR (CCl_4) ($CDCl_3$) δ_H 5.32, Wh/2 8 Hz, H7; 1.61 (br), Me. lit. cit.[13] δ_H 5.27. ^{13}C NMR ($CDCl_3$) δ_C 139.8, C6; 122.7, C7; 19.2, Me and **12** ^1H NMR ($CDCl_3$) δ_H 4.58, Wh/2 3 Hz, (H11)$_2$. lit. cit.,[13] ^1H NMR (CCl_4) δ_H 4.54. ^{13}C NMR δ_C 104.3, C11; 155.4, C6. Compound **5a** was present < 2% ^1H NMR δ_H 1.05, however the mixture of **11** and **12** on standing in $CDCl_3$ for two weeks rearranged to **5a** in high yield (> 80%).

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