

^1H N.m.r. Spectra of some Bicyclic Compounds

I—Relative Configurations of the Diastereomeric *endo*- α -Methyl-5-norbornene-2-methanols, the Corresponding Saturated Analogues, and their Cyclization Ether Products

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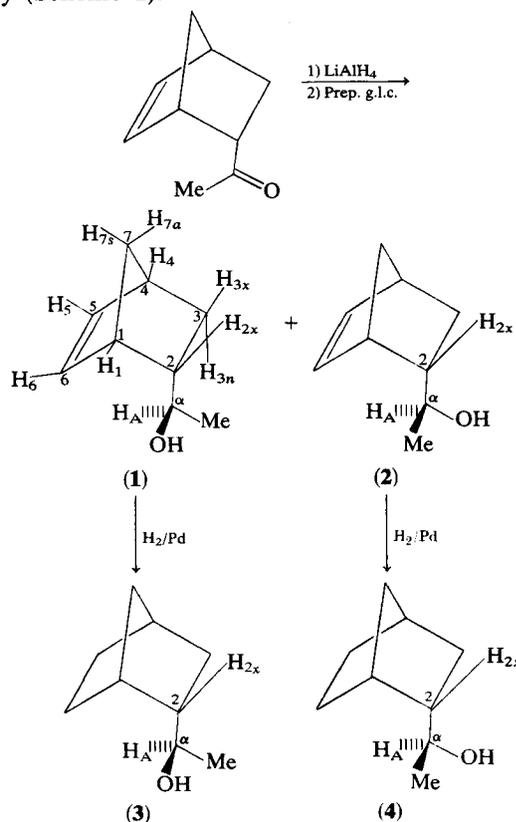
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The configurational and conformational relationship at C-2 and C- α in the two racemic diastereomeric *endo*- α -methyl-5-norbornene-2-methanols and the corresponding saturated *endo*- α -methyl-2-norbornanemethanols were determined by first-order analysis of the ^1H n.m.r. spectra of these compounds and of their cyclization ether products, i.e. 3-methyl-2-oxatricyclo[4.2.1.0^{4,5}]nonanes and 5-methyl-4-oxatricyclo[4.3.0.0^{3,8}]nonanes. In addition, the conformational preference of the hydroxyl group in the unsaturated and saturated alcohols was confirmed by the lanthanide induced shift technique, using Eu(fod)₃ as shift reagent, combined with a computer program involving various conformations of the -CHOHMe group.

In connection with studies concerning reactions of some bicyclic compounds, the two racemic diastereomers of *endo*- α -methyl-5-norbornene-2-methanol (1 and 2) and of the corresponding saturated *endo*- α -methyl-2-norbornanemethanol (3 and 4) were prepared and separated by preparative gas chromatography (Scheme 1).



Scheme 1†

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RESULTS AND DISCUSSION

^1H n.m.r. spectra

The ^1H 220 MHz n.m.r. (CDCl_3) spectra of the unsaturated alcohols 1 and 2 have been completely assigned on the basis of the chemical shifts and coupling constants by first order analysis (Tables 1 and 2). These assignments were also confirmed by decoupling

Table 1. ^1H chemical shifts^a (δ) (i) and experimental LIS values^b (ii) for alcohols 1-4

Protons ^c	1		2		3		4	
	i	ii	i	ii	i	ii	i	ii
1	3.01	12.90	2.77	7.60	2.31	14.00	2.13	8.20
2x	1.99	15.10	2.00	15.50		17.30		19.60
3x	1.77	6.70	1.85	9.60				11.20
3n	0.50	9.10	0.92	13.60	0.55		0.96	15.00
4	2.78	3.40	2.82	3.20	2.16	3.20	2.21	4.20
5	6.13	3.70	6.16	3.20				
6	6.03	8.90	5.89	4.80		13.30(6n)		
7a	1.23	4.40	1.26	4.50				
7s	1.43	3.60	1.41	2.80				
A	3.13	25.25	3.16	23.00	3.52	27.80	3.54	28.40
Me	1.13	14.20	1.20	14.00	1.17	15.10	1.19	16.50

^a Measured from 220 MHz n.m.r. spectra (CDCl_3).

^b Extrapolated for SR/S = 1/1.

^c Abbreviations: x = *exo*, n = *endo*, s and a = *syn* and *anti* (with respect to C-5 and C-6), A = hydrogen attached to C- α (see Scheme 1).

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† Abbreviations used for designating hydrogens: x = *exo*, n = *endo*, s and a = *syn* and *anti* (with respect to C-5 and C-6), A = hydrogen attached to C- α .

Table 2. Couplings (Hz)^a in alcohols 1-4

Protons ^b	1	2	3	4
2x,3x	9.4	9.0		
2x,3n	4.3	3.6	3.5	4.5
3x,3n	-11.3	-11.0	-11.5	-11.5
4,5	3.0	3.0		
5,6	5.7	5.6		
1,6	3.0	2.7		
3n,7s ^c	2.5	2.5	2.0	2.5
7a,7s	-8.3	-8.5		
A,2x	10.0	9.0	10.0	9.7
A,Me	6.2	6.2	6.0	6.0

^a Measured from expanded ¹H 220 MHz n.m.r. spectra (CDCl₃), sweep width 250 Hz for 1 and 2 and 500 Hz for 3 and 4.

^b See footnote ^c to Table 1.

^c Apart from *J*(7a,7s) and *J*(3n,7s), signal H-7s is split by two additional couplings (2.0–2.5 Hz each).

experiments and the use of the lanthanide induced shift (LIS) technique (see next Section). The complexity of the ¹H 220 MHz n.m.r. spectra of the saturated alcohols 3 and 4 allowed only partial assignments (Tables 1 and 2). The similarity of the coupling between H-A and H-2x [*J*(2x,A) = 9–10 Hz] in compounds 1–4 with axial-axial coupling observed in rigid cyclohexanoic systems in which one carbon involved bears an oxygen substituent,¹ indicates that alcohols 1–4 exist predominantly in conformations in which the spatial orientation of H-2x and H-A is very close to the *anti* arrangement (Fig. 1). For one diastereomeric form (1 and 3 or 2 and 4) this preferred conformation is I and for the other (2 and 4 or 1 and 3) it is II. It should be noted that these conformers are also favoured for steric reasons.

Such different geometrical relationships of the substituents (OH, Me) at C- α with respect to the bicyclic system in the two diastereomeric forms having conformation I and II, respectively, should result in different anisotropic effects due to the hydroxyl and methyl groups. This could then possibly explain the large downfield shift (c. 0.40 ppm) of the H-3n signal in alcohols 2 and 4 from the usual positions,² c.f. alcohols 1 and 3. [Actually the H-3n signal of alcohol 1 appears to be slightly displaced downfield (with respect to the corresponding signal in more simple systems),² possibly because of the 1,3 influence of the α -methyl group.³] The same explanation could account for the (smaller) downfield displacement of the H-1 signal in alcohols 1 and 3 (0.24–0.18 ppm) and of the H-6 signal in alcohol 1 (0.14 ppm). If these effects are due, as expected, to the influence of the hydroxyl group⁴ rather than the methyl group,³ 1 and 3 would have the

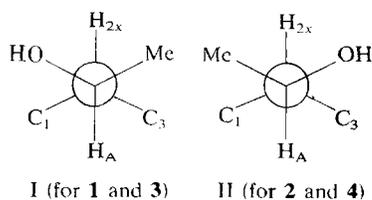
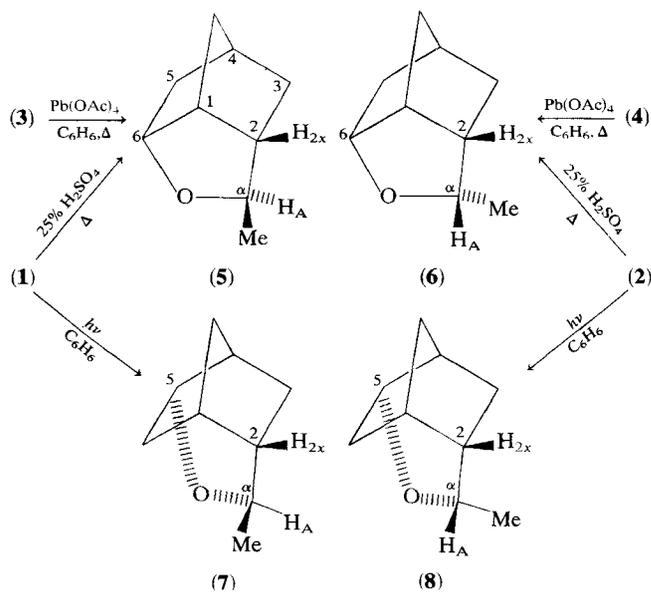


Figure 1. Configurational and conformational relationship at C- α and C-2 in alcohols 1-4.

stereochemistry of conformer I, i.e. the 2*S*, α R or 2*R*, α S configuration, and 2 and 4 that of conformer II, i.e. the 2*S*, α S or 2*R*, α R configuration (see Fig. 1 and Scheme 1).

In order to verify this tentative assignment of stereochemistry for 1–4, the ¹H 60 MHz n.m.r. spectra of their cyclization products, i.e. the two epimeric 3-methyl-2-oxatricyclo[4.2.1.0^{4,8}]nonanes (5 and 6) and the two epimeric 5-methyl-4-oxatricyclo[4.3.0.0^{3,8}]nonanes (7 and 8), prepared according to Scheme 2, were studied. In these ethers the



Scheme 2

conformations of, and therefore the dihedral angles (τ) in, the side chain are fixed and the configuration at C- α corresponds to that of the alcohols from which they are derived. (Although the cyclic ethers 5–8 are properly named according to the IUPAC nomenclature, for reasons of simplicity the same norbornane numbering system as that for alcohols 1–4 has been employed in the discussion of their n.m.r. spectra).

The ¹H n.m.r. data of ethers 5–8 obtained by first-order analysis (Table 3) are consistent with previous

Table 3. ¹H n.m.r. data of ethers 5–8

Protons ^a	5	6	7	8
Chemical shifts (δ) ^b				
A	3.92	3.92	3.95	4.11
5x			4.14	4.08
6x	4.32	4.15		
1	2.70	2.70		
Me	1.04	1.12	1.31	1.13
Couplings (Hz) ^c				
2x,A	0.0	3.6	2.3	0.5–1.0
2x,Me	6.3	6.4	6.9	6.2
5x,6x			5.1	5.3
5x,1			2.0	2.2
5x,4			5.1	5.3

^a See footnote ^c to Table 1, and Scheme 2.

^b Measured from 60 MHz n.m.r. spectra (CCl₄ for 5 and 6 and CDCl₃ for 7 and 8).

^c Measured from expanded 60 MHz n.m.r. spectra (sweep width 100 Hz).

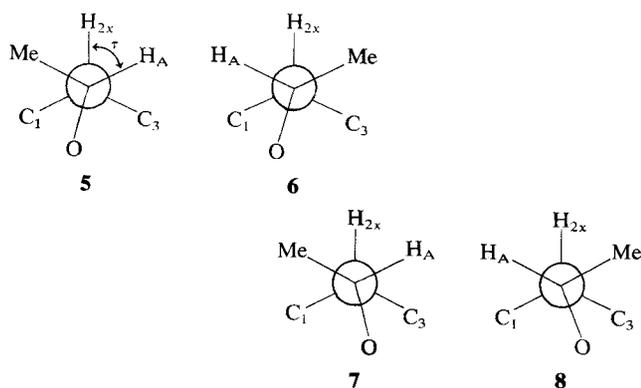


Figure 2. Newman representations of the C- α —C-2 fragment in ethers 5-8 (one enantiomer shown).

n.m.r. studies of related systems.^{5,6} A recent method⁷ for calculation of dihedral angles (τ) from *gauche* vicinal coupling constants and substituent electronegativities was applied for the calculation of $\tau_{2x,A}$ in ethers 5-8. Thus, in the spectrum of the 5-membered cyclic ether 5, obtained from alcohols 1 and 3, the coupling between H-2x and H-A [$J(2x,A) = 0.0$ Hz] corresponds to a *trans*-H-2x,H-A arrangement ($\tau_{2x,A} = 79^\circ$), whereas in the spectrum of the epimeric 5-membered cyclic ether 6, derived from alcohols 2 and 4, this coupling [$J(2x,A) = 3.6$ Hz] is in accordance with a *cis*-H-2x,H-A geometry ($\tau_{2x,A} = 48^\circ$) (Fig. 2). Similarly, from the ¹H n.m.r. spectra of the 6-membered cyclic photoethers 7 and 8, one obtains: $J(2x,A) = 2.3$ Hz, $\tau_{2x,A} = 55^\circ$ for ether 7, the cyclization product of alcohol 1, and 0.5 Hz $< J(2x,A) < 1.0$ Hz, $67^\circ < \tau_{2x,A} < 72^\circ$ for ether 8, derived from alcohol 2 (Fig. 2).

From these results it follows that ethers 5 and 7, and therefore alcohols 1 and 3, have the 2*S*, α *R* or 2*R*, α *S* configuration (alcohols 1 and 3 being predominantly in conformation I), and ethers 6 and 8, and therefore alcohols 2 and 4, have the 2*S*, α *S* or 2*R*, α *R* configuration (alcohols 2 and 4 existing preferentially in conformation II).

LIS analysis

The method applied in the LIS analysis of alcohols 1-4 was similar to that used in the LIS studies of the racemic diastereomeric tricarbonyl-(3,5-heptadien-2-ol)iron complexes⁹ and flexible chains fastened to a rigid core.^{10,11} It should be noted that only a few norbornene derivatives (including some 5-norbornene-2-methanols) have been analysed so far by the LIS technique.⁸

The induced chemical shifts of alcohols 1-4 were obtained by the incremental addition of known weights of solid Eu(fod)₃ as shift reagent (SR) to a 0.7 M carbon tetrachloride solution of substrate (S), containing 2-5% of TMS, and by subsequent shift measurements from the ¹H 60 MHz spectra. Plots of the induced shifts vs the molar ratio SR/S gave a linear relationship in the range SR/S = 0.2-0.5. In the unsaturated epimeric alcohols (1 and 2) the induced shifts were obtained for all protons, whereas the complexity of the spectra of the saturated alcohols (3 and

4), even for a high SR/S, allowed only partial assignment. The LIS values listed in Table 1, which were used in the calculations, are extrapolated values for SR/S = 1.¹²

Almost all the differences in chemical shifts of the corresponding protons in the diastereomeric alcohols 1 and 2, and 3 and 4, were much increased by the addition of the shift reagent (Table 1), this being due to changes in the steric relationship of the coordination site (OH group) to the bicyclic skeleton. It was also established that couplings, including $J(2x,A)$, were not appreciably affected by the presence of SR.

The computer program PDJGM¹³ was used to fit the calculated $(3 \cos^2 \theta - 1)/r^3$ LIS values to the observed ones. The geometry of *endo*-5-norbornen-2-ol^{13,14} and the electron diffraction data for norbornane¹⁵ were used as input for the skeletons of the unsaturated alcohols (1 and 2) and saturated alcohols (3 and 4), respectively. The -C-OH fragment was attached to the 2-*endo* position by the standard tetrahedral geometries. The conformers were generated by 360° rotation in 20° increments around the C-2—C- α bond, which was fixed in the +x, -z plane of a right handed Cartesian coordinate system (Fig. 3). As in the original paper,¹⁴ oxygen was placed at the origin and the C- α —O bond along the negative z axis.

For each step (ψ_n), the lanthanide was moved incrementally over the surface of a limited sphere ($\rho = 0-100^\circ$; $\Delta\rho = 10^\circ$; $\phi = 0-360^\circ$; $\Delta\phi = 360/\rho^\circ$; Eu—O = 2.9 Å) and the agreement factor calculated.¹³ The minimum agreement factors R for each conformer-data set pair are listed in Table 4. The similarity of the shapes of the curves (not shown) obtained from these data for alcohols 1 and 3, and for 2 and 4, respectively, constitutes evidence that these compounds exhibit the same conformational preferences. (ψ_{\min} is the dihedral angle corresponding to the minimum (best) value of the agreement factor R.) In alcohols 1 ($\psi_{\min} = 200^\circ$) and 3 ($\psi_{\min} = 180^\circ$) the OH group is *gauche* to C-1 and H-2x, whereas in alcohols 2 ($\psi_{\min} = 80^\circ$) and 4 ($\psi_{\min} = 80^\circ$) the same group is *gauche* to

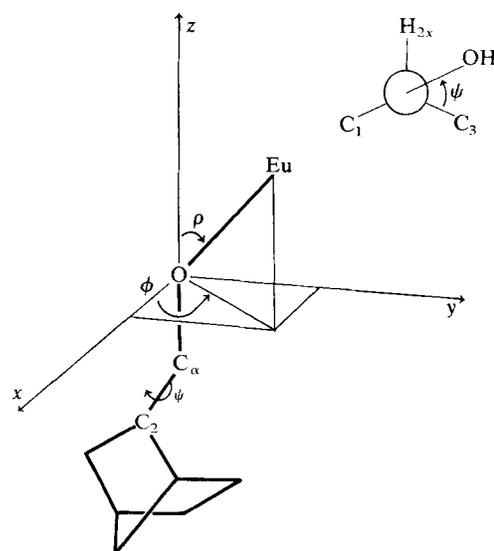


Figure 3. The substrate and shift reagent as described with respect to the internal coordinate system.

Table 4. Minimum agreement factor R^a (%) vs conformer (ψ)^b for Eu—O = 2.9 Å

Conformer (ψ°)	1	2	3	4
0	56.0	36.9	29.3	42.9
20	53.9	32.4	22.1	38.3
40	47.9	23.8	21.0	28.9
60	39.3	12.0	22.9	16.5
80	29.7	7.4	25.2	1.3
100	26.7	14.3	25.7	7.4
120	24.5	19.3	23.2	13.6
140	20.5	21.9	17.4	17.0
160	14.8	22.2	8.9	17.8
180	9.6	20.8	2.6	15.9
200	5.9	21.6	8.9	11.2
220	7.9	21.5	41.6	7.2
240	33.3	51.3	55.2	8.9
260	44.3	60.3	64.4	14.9
280	45.2	58.1	65.5	22.9
300	42.0	37.1	61.8	31.0
320	47.2	32.2	54.3	38.1
340	53.8	36.5	44.1	42.6

^a $R = [\sum w(\text{obs.} - \text{calc.})^2 / \sum w(\text{obs.})^2]^{1/2}$, $w = 1$.

^b $\angle \text{C}-\text{C}-\text{C}-\text{C}-\alpha-\text{OH}$.

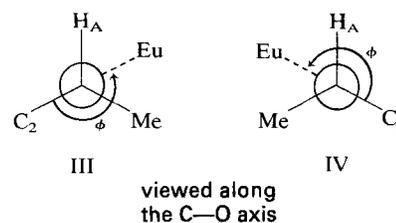
C-3 and H-2x. Incorporation of the information available from $J(2x\text{A})$ leads to the configurations of alcohols **1-4** (Scheme 1, Fig. 1) which are entirely consistent with the assignment based on ^1H n.m.r. spectra (see first Section).

Proton H-A and the Me group have been attached according to the configurations assigned (Fig. 1, I and II) and a second set of calculations was carried out for conformers selected within the ranges $\psi_{\text{min}} \pm 20^\circ$ ($\rho = 0-100^\circ$, $\Delta\rho = 10^\circ$; $\phi = 0-360^\circ$, $\Delta\phi = 360/\rho^\circ$; Eu—O = 2.5–3.3 Å, $\Delta \text{Eu—O} = 0.2 \text{ Å}$). The minimum values of the agreement factor R , i.e. the minima of graphs of R vs ψ for various Eu—O distances (not shown), are distributed over the ranges $\psi_{\text{min}} = 5-15^\circ$ (Table 5). In all cases the shift reagent complex consis-

Table 5. Minimum agreement factors R_{min} and corresponding Eu positions for alcohols **1-4**

	Eu—O distance (Å)				
	2.5	2.7	2.9	3.1	3.3
Alcohol 1					
α^{oa}	160	160	160	160	160
ϕ^{oa}	180	195	210	225	240
ψ^{oa}	210	210	205	205	200
$R_{\text{min}}(\%)$	4.6	4.2	4.3	4.5	4.7
Alcohol 2					
α°	150	150	150	150	150
ϕ°	160	150	150	140	130
ψ°	70	70	75	75	75
$R_{\text{min}}(\%)$	5.6	4.9	4.8	4.6	4.6
Alcohol 3					
α°	120	120	120	110	110
ϕ°	200	195	175	160	150
ψ°	185	180	170	170	170
$R_{\text{min}}(\%)$	1.9	3.9	4.6	5.7	7.6
Alcohol 4					
α°	150	150	140	140	140
ϕ°	160	160	176	160	130
ψ°	75	80	85	85	85
$R_{\text{min}}(\%)$	2.7	1.9	1.7	2.5	3.0

^a $\alpha = \angle \text{C}-\alpha-\text{O}-\text{Eu}$, $\phi = \angle \text{C}-2-\text{C}-\alpha-\text{O}-\text{Eu}$, $\psi = \angle \text{C}-3-\text{C}-2-\text{C}-\alpha-\text{OH}$; see also Figs. 3 and 4.



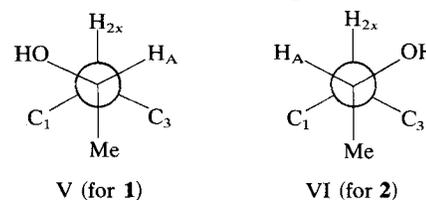
(1) $\phi = 180-240^\circ$
(3) $\phi = 150-200^\circ$

(2) $\phi = 130-160^\circ$
(4) $\phi = 130-160^\circ$

Figure 4. The positions of Eu ion in the complexed substrates (Table 5).

tently avoids the most hindered regions (Fig. 4, III and IV).

Similar calculations, using experimental LIS data of **1** and **2**, were also carried out for conformers V ($\psi = 200^\circ$) and VI ($\psi = 75^\circ$) (Fig. 5), which are pro-

**Figure 5. Conformers of alcohols **1** and **2** generated by 'epimerization' (I \rightarrow V and II \rightarrow VI), i.e. having the 'wrong' configuration at C- α .**

duced by reversing the positions of H-A and Me in I and II, i.e. by interconverting the configuration at C- α in the diastereomeric alcohols **1** and **2**. The variations of ρ , ϕ and Eu—O were the same as those used above.

The best values of the agreement factor R and the corresponding Eu positions obtained from these calculations are listed in Table 6. As far as the LIS analysis alone is concerned, the results obtained by using 'wrong' configurations (as in V and VI) for **1** and **2** could be quite acceptable. Such solutions are, however, strongly denied for steric reasons (Me occupies the most hindered position) and by the information obtained from $J(2x\text{A})$. The insensitivity of the LIS analysis to the configurational change at C- α is in accordance with previous results.^{9,11}

Clearly, there still remains the question as to whether the agreement factor R could be improved by changing the geometry of the skeleton, since, as shown recently on some norbornane derivatives,¹⁶ the choice of the ring geometry can affect the R value considerably.

Table 6. Minimum agreement factors R_{min} and corresponding Eu positions for conformers V and VI

	Eu—O distance (Å)				
	2.5	2.7	2.9	3.1	3.3
Conformer V					
α^{oa}	150	160	150	140	130
ϕ^{oa}	180	180	200	210	210
ψ^{oa}	200	200	200	200	200
$R_{\text{min}}(\%)$	5.0	4.6	5.0	6.1	7.4
Conformer VI					
α°	160	150	150	140	150
ϕ°	180	160	150	144	150
ψ°	75	75	75	75	75
$R_{\text{min}}(\%)$	6.6	6.0	5.2	4.7	5.0

^a See footnote to Table 5.

EXPERIMENTAL

Infra-red spectra were recorded as liquid films with a Perkin-Elmer Grating Spectrophotometer Model 337. N.m.r. spectra were obtained on a Varian A 60A, a Perkin-Elmer R12B (in the LIS analysis) and a Varian HR 220 (PCMU Harwell) spectrometer. Analytical and preparative g.l.c. were carried out on a Varian Aerograph instrument Series 1200 and a Varian Aerograph instrument Model A-700, respectively, using the columns specified. Mass spectra and accurate mass measurements were obtained on a Varian-Atlas MAT CH 5. Elemental microanalysis of all new compounds gave satisfactory percentage values for C and H.

Calculations (in the LIS analysis) were carried out using the Fortran IV PDIGM program¹³ on an ICL 1905E machine (LPCU—The Polytechnic of North London). The original program was supplied subsequently (J. Waite and A. P. Johnson, Polytechnic of North London) with a subroutine which converts input bond lengths and angles into atomic coordinates.

Reduction of *endo*-2-acetyl-5-norbornene

To a stirred solution of lithium aluminium hydride (0.313 g, 8.2 mmol) in dry ether (10 ml) was added dropwise a solution of *endo*-2-acetyl-5-norbornene¹⁷ (4.08 g, 30 mmol) in the same solvent (40 ml). After 2 h of reflux, the cooled mixture was worked up by addition of water and 10% sulphuric acid. The ethereal extracts were washed with aqueous saturated sodium bicarbonate and water, and dried over anhydrous magnesium sulphate. The removal of solvent *in vacuo* afforded a pale yellow oil (3.90 g, 94%) which was a mixture of **1** (43%) and **2** (57%) (g.l.c.: 10% TCEP on Chromosorb P 60–80, 200 × 0.2 cm, Ar, 110 °C). The unsaturated alcohols **1** and **2** were separated by preparative g.l.c. (20% TCEP on Chromosorb P 60–80, 300 × 0.9 cm, H₂, 120 °C).

***endo*-α-Methyl-5-norbornene-2-methanol** (diastereomer **1**), colourless oil, n_D^{20} 1.4913, shorter t_R . i.r.: ν_{\max} 3360, 3070, 1567, 1370, 1090, 730 cm⁻¹; m.s.: parent ion C₉H₁₄O m/e 138.10532, base peak (retro Diels-Alder) C₅H₆ m/e 66.

***endo*-α-Methyl-5-norbornene-2-methanol** (diastereomer **2**), m.p. 34–35 °C, longer t_R . i.r.: ν_{\max} 3270, 3070, 1567, 1104, 730 cm⁻¹; m.s.: parent ion C₉H₁₄O m/e 138.10532, base peak (retro Diels-Alder) C₅H₆ m/e 66.

Hydrogenation of the unsaturated alcohols **1 and **2****

The procedure used was similar to that described for hydrogenation of 2-acetyl-5-norbornene.¹⁸ To a suspension of 0.10 g of 10% Pd on C in ethanol (25 ml) was added the unsaturated alcohol **1** or **2** (0.50 g, 3.6 mmol). The mixture was stirred for 1 h at 40 lb in⁻² of hydrogen, filtered and the solvent removed under reduced pressure to give a pale yellow oil which consisted of one major component (>95%) (g.l.c., same conditions as above). Analytically pure samples of the products were obtained by preparative g.l.c. (same conditions as above).

***endo*-α-Methyl-2-norbornanemethanol** (diastereomer **3**), obtained from **1**, m.p. 36–38° (shorter R_f). i.r.: ν_{\max} 3320, 1370, 1098, 896 cm⁻¹; m.s.: (parent ion —H₂O) C₉H₁₄ m/e 122.10957, base peak (parent ion —C₂H₅O) C₇H₁₁ m/e 95.

***endo*-α-Methyl-2-norbornanemethanol** (diastereomer **4**), obtained from **2**, colourless oil, n_D^{20} 1.4835 (longer R_f). i.r.: ν_{\max} 3360, 1370, 1120, 1080, 744 cm⁻¹; m.s.: (parent ion —H₂O) C₉H₁₄ m/e 122.10955, base peak (parent ion —C₂H₅O) C₇H₁₁ m/e 95.

Acid catalysed cyclization of the unsaturated alcohols **1 and **2****

The procedure was similar to that described for the cyclization of other unsaturated alcohols.¹⁹ The unsaturated alcohol **1** or **2** (0.50 g, 3.6 mmol) and aqueous 25% sulphuric acid (v/v, 2 ml) were stirred on a water bath for 3 h. The products were extracted with ether, the ethereal extracts washed with aqueous saturated sodium bicarbonate and water, and dried over anhydrous magnesium sulphate. After evaporation of the solvent a pale yellow residue was obtained containing about 75% (g.l.c., same conditions as above) of the cyclization product, which was purified by preparative g.l.c. (same column as above, 110 °C).

3-Methyl-2-oxatricyclo[4.2.1.0^{4,8}]nonane (diastereomer **5**), obtained from **1**, colourless liquid, n_D^{20} 1.4751 (shorter R_f). i.r.: ν_{\max} 1380, 1150, 1142, 1089, 1075, 1041, 1012 cm⁻¹; ms: parent ion C₉H₁₄O m/e 138.10447, base peak (parent ion —CH₃) C₈H₁₁O m/e 123.

3-Methyl-2-oxatricyclo[4.2.1.0^{4,8}]nonane (diastereomer **6**), obtained from **2**, colourless liquid, n_D^{20} 1.4772 (longer R_f). i.r.: ν_{\max} 1388, 1151, 1131, 1098, 1080 cm⁻¹; m.s.: parent ion C₉H₁₄O m/e 138.10510, base peak (parent ion —CH₃) C₈H₁₁O m/e 123.

Lead tetraacetate oxidation of the saturated alcohols **3 and **4****

The oxidations were carried out according to a general procedure reported previously.²⁰ The saturated alcohol **3** or **4** (0.50 g, 3.6 mmol) was treated with lead tetraacetate (1.68 g, 3.6 mmol + 5% excess) in refluxing dry benzene (50 ml) in the presence of anhydrous calcium carbonate (0.40 g, 3.6 mmol + 10% excess) until the disappearance of tetravalent lead (about 5 h). After the usual work up²⁰ and removal of the solvents, the reaction products were separated and isolated by preparative g.l.c. (same conditions as above). The cyclic ether obtained in 53% yield from alcohol **3** was identical to **5**, and the cyclic ether obtained in 57% yield from alcohol **4** was identical to **6** (see above).

Ultra-violet irradiation of the unsaturated alcohols **1 and **2****

The procedure used for these photolytic reactions was similar to that described previously.⁵ A stirred solution of the unsaturated alcohol **1** or **2** (0.88 g, 6.3 mmol) in dry deaerated benzene (330 ml), through which a stream of dry nitrogen was bubbled (during the whole reaction), was irradiated for 7 h with a Baird and

Tatlock 400 W medium pressure mercury arc placed in a water-cooled immersion well. After removal of the solvent (by fractional distillation under normal pressure), the photoether product in the residue was separated by preparative g.l.c. (10% Carbowax 20 M on Chromosorb W 60–80, 200×0.9 cm, N_2 , $150^\circ C$).

5-Methyl-4-oxatricyclo[4.3.0.0^{3,8}]nonane (diastereomer **7**), obtained in 66% yield (pure) from **1**, colourless liquid, n_D^{20} 1.4922 (longer R_f using 10% TCEP on Chromosorb P 60–80, 200×0.2 cm, N_2 , $80^\circ C$). i.r.: ν_{max} 1380, 1164, 1098, 1090, 1052, 1012, 1000, 982, 784 cm^{-1} ; m.s.: parent ion $C_9H_{14}O$ m/e 138.10494, base peak (parent ion $-C_2H_4O$) C_7H_{10} m/e 94.

5-Methyl-4-oxatricyclo[4.3.0.0^{3,8}]nonane (diastere-

omer **8**), obtained in 59% yield (pure) from **2**, colourless liquid, n_D^{20} 1.4891 (shorter R_f). i.r.: ν_{max} 1390, 1160, 1100, 1043, 1020, 985, 968, 804 cm^{-1} ; m.s.: parent ion $C_9H_{14}O$ m/e 138.10500, base peak (parent ion $-C_2H_4O$) C_7H_{10} m/e 94.

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