The ^{1}H Nuclear Magnetic Resonance Spectra of 6-Substituted Bicyclo-[3.1.0]hex-2-enes

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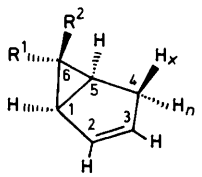
^{1}H N.m.r. spectroscopy can readily distinguish *endo*- and *exo*-6-substituted bicyclo[3.1.0]hex-2-enes. Nuclear Overhauser measurements coupled with resolution enhancement techniques and T_1 values have permitted a full assignment of the ^{1}H n.m.r. parameters.

6-SUBSTITUTED bicyclo[3.1.0]hex-2-enes are useful intermediates in prostaglandin synthesis [1,2] and have also been used in studies of the mechanistic aspects of carbonium ion rearrangements.[3,4] An example of the molecular interconversions which this bicyclic skeleton can undergo is provided by *endo*-6-formylbicyclo[3.1.0]hex-2-ene (2; X = O). This aldehyde (2; X = O) has been shown [5] to exist in equilibrium with 2-oxabicyclo[3.2.1]-octa-3,6-diene (1; X = O) through a Cope rearrangement. It can also readily be epimerised [6] to the *exo*-aldehyde (3; X = O). We have recently described the syntheses and properties of the 2-heterabicyclo[3.2.1]-octa-3,6-dienes (1; X = O, S, NR) and demonstrated the equilibrium (1) ⇌ (2) for cases where X = NR.[7,8] In the course of this work we prepared a series of new 6-substituted bicyclo[3.1.0]hex-2-enes (4) and (5) and found a lack of precise ^{1}H n.m.r. reference data on these compounds. This complicated structural assignments in this important area and so we now report a full assignment of the chemical shifts and coupling constants for the *endo*- and *exo*-sulphonamides (4a) and (5a), respectively. This has proved useful in making assignments to related compounds in the series.

(1) (2) (3)



(4) *endo*

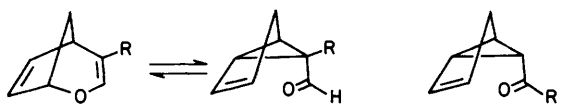
a; R^1 = H, R^2 = CH_2NHSO_2Ph
b; R^1 = H, R^2 = $CHD \cdot NHSO_2Ph$
c; R^1 = H, R^2 = CH_2NH_2
d; R^1 = H, R^2 = CH_2OH
e; R^1 = H, R^2 = $CHD \cdot OH$
f; R^1 = H, R^2 = CD_2OH
g; R^1 = D, R^2 = CH_2OH
h; R^1 = Me, R^2 = CH_2OH
i; R^1 = Cl, R^2 = CH_2OH
j; R^1 = H, R^2 = $CH(OH)SO_3Na$
k; R^1 = D, R^2 = $CH(OH)SO_3Na$
l; R^1 = H, R^2 = $CD(OH)SO_3Na$

(5) *exo*

a; R^1 = CH_2NHSO_2Ph, R^2 = H
b; R^1 = CH_2NH_2, R^2 = H
c; R^1 = CH_2OH, R^2 = H
d; R^1 = $CH(OH)SO_3Na$, R^2 = H

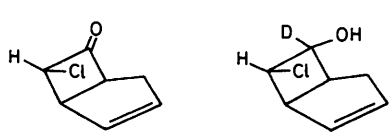
Syntheses.—In the *endo*-series, compounds (4a—d and j) were prepared by previously reported methods.[5,7] Alcohols (4h and i) were obtained by sodium borohydride reduction of the corresponding known [9,10] aldehydes (7a and b), respectively. The (7*RS*)-[7-$^2H_1$]alcohol (4e) and [7-$^2H_2$]alcohol (4f) were prepared by reduction of the aldehyde (2; X = O) and acid (8a),[11] respectively, with lithium aluminium deuteride. Base-catalysed deuterium exchange of the aldehyde (2; X = O) at room temperature gave the [6-^{2}H]-*endo*-aldehyde (7c) which on reduction with sodium borohydride yielded the [6-^{2}H]-alcohol (4g). The deuteriated aldehyde (8b), required for preparation of the hydrogen sulphite adduct (4l), was obtained by suitable modification of the route used by Brook.[9] Thus sodium borodeuteride reduction of the known [12] chloroketone (9) gave the *endo*-alcohol (10). This, on brief treatment with 2N-sodium hydroxide solution, underwent rearrangement to the desired aldehyde (8b).

Access to the *exo*-series of compounds (5) was made *via* the known [6] *exo*-aldehyde (3; X = O), which was readily obtained from the *endo*-aldehyde (2; X = O) by base-



(6) (7) (8)

(6) a; R = Me; b; R = Cl; c; R = D
(8) a; R = OH; b; R = D



(9) (10)

catalysed epimerisation. Conversion of the aldehyde (3; X = O) into its oxime (3; X = NOH) followed by reduction to the amine (5b) and treatment with benzenesulphonyl chloride yielded the *exo*-sulphonamide (5a). Sodium borohydride reduction of the aldehyde (3; X = O) yielded the *exo*-alcohol (5c).

Ambiguity remained over the assignment of H-2 and -3. The fact that H-6 is long-range-coupled to the higher field olefinic signal with J 0.40 Hz but not to the lower field signal suggests that the higher field signal (δ 5.34) can be assigned to H-2, but then from the full coupling constant analysis $J_{1,2}$ becomes 0.34 Hz and $J_{1,3}$ becomes 2.07 Hz, an unexpected situation. This would argue for a reversal of the assignments of H-2 and -3. N.O.e. experiments were now performed to resolve this problem and also to determine the assignments of H-4*x* and -4*n* unequivocally. H-1 and -5 had been assigned on the basis of their coupling to H-4 and, in an n.O.e. experiment, irradiating H-1 gave a positive enhancement on only one olefinic proton resonance. This confirmed the assignment of H-1 and showed that H-2 was the lower field of the two olefinic hydrogens and there was 1,6-long-range coupling between H-3 and -6 but not 1,5- long-range coupling between H-2 and -6.

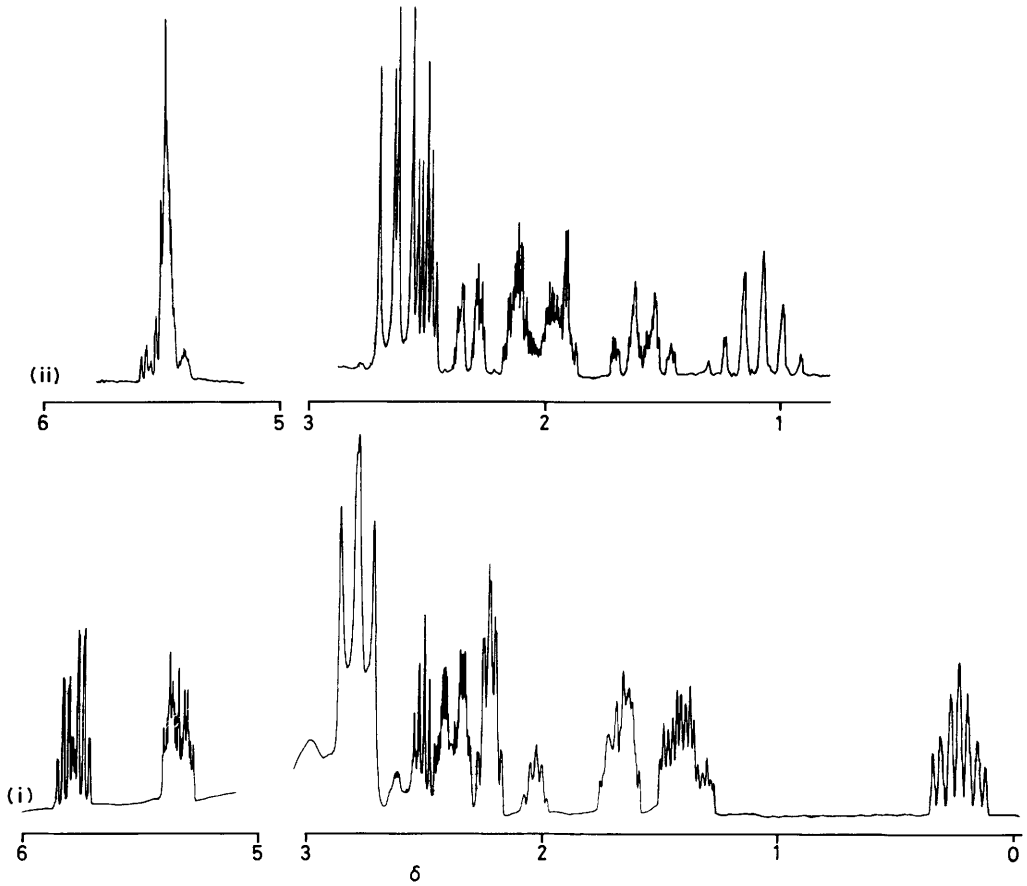


FIGURE 1 90 MHz ^{1}H N.m.r. spectra of (4a) and (5a) in degassed [$^2H_6$]DMSO at 100 °C: (i) *exo*-isomer (5a); (ii) *endo*-isomer (4a). The aromatic resonances are folded into the frequency gap between aliphatic and olefinic resonances and are not shown

Spectral Assignments.—The exo-*sulphonamide* (5a). The 90 MHz ^{1}H n.m.r. spectrum of this compound dissolved in [$^2H_6$]DMSO is shown in Figure 1(i). Expanded resolution-enhanced traces of each band are given in Figure 2. Some assignments were straightforward, notably the methylene at C-7 and the methine at C-6. Ambiguity existed in the assignment of resonances for the following pairs: H-2–H-3, H-4*x*–H-4*n*, H-1–H-5. Many long-range couplings were observed and in most cases these could be assigned easily from pairing the couplings on two bands. Even after analysis of the multiplicities however, some ambiguities remained.

One band due either to H-1 or H-5 is seen to contain two large couplings of 6.59 and 6.26 Hz. The smaller coupling appears on the other nucleus of the pair, H-5 or -1, and the larger coupling is paired with a splitting on H-4*x* or -4*n*. This is more in keeping with the vicinal coupling $J_{4,5}$ rather than the four-bond coupling $J_{1,4}$ and H-1 and -5 have been assigned accordingly.

Saturation of H-5 gave no n.O.e. at either H-2 or -3 but an effect appeared on the low-field half of the pattern due to H-4*x* and -4*n*. Inspection of a Dreiding model shows that H-5 is much closer to H-4*n* than to H-4*x* and this confirms the assignment of these resonances. All the ^{1}H n.m.r. assignments are collected together in

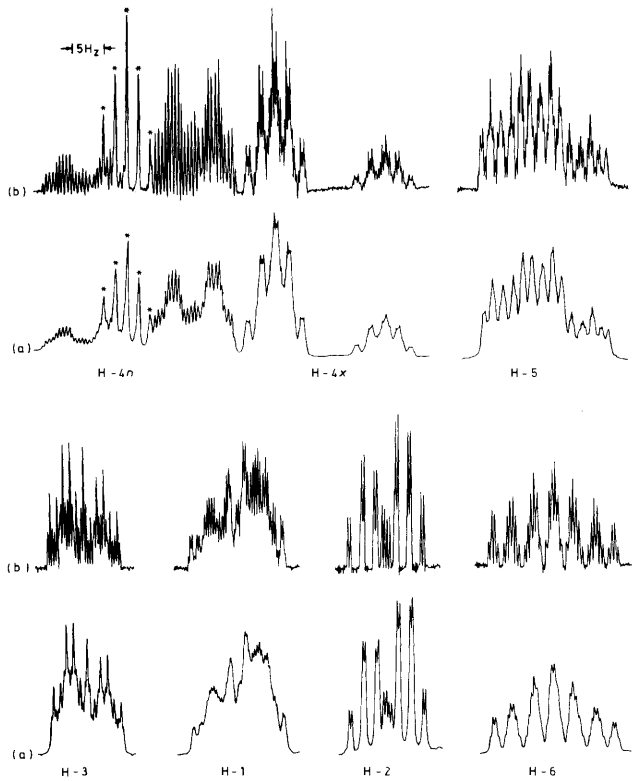


FIGURE 2 Resolution-enhanced 90 MHz ^{1}H n.m.r. spectra of the *exo*-isomer (5a): (a) no exponential weighting applied to the f.i.d.; (b) after application of the optimum Gaussian weighting function

Table 1 and additional evidence for these is provided by the relaxation-time measurements as follows:

Nucleus	T_1/s
H-1	6.4
H-2	7.1
H-3	6.1
H-4*x*	5.0
H-4*n*	4.0
H-5	5.0
H-6	4.6
CH_2	3.1
NH	2.1

These relaxation times are in keeping with the assignments since: (i) the T_1 value for H-5 would be expected to be shorter than that for H-1 because H-5 will be relaxed more efficiently by the two vicinal hydrogens H-4*x* and -4*n* compared to the one vicinal H-2 for H-1 relaxation; (ii) similarly the T_1 value for H-3 should be shorter than that for H-2; and (iii) the T_1 values of H-4*n* should be shorter than that of H-4*x* because the distance H-4*n*–H-5 is less than H-4*x*–H-5.

Further inspection of the coupling constants given in Table 1 also supports the assignments of the chemical shifts because: (i) the vicinal coupling $J_{1,2}$ becomes 2.07 Hz and the longer range $J_{1,3}$ becomes 0.34 Hz. (ii) The coupling constant $J_{4n,5}$ now becomes that between *cis*-hydrogens having a value of 6.60 Hz whilst the *trans*-coupling constant $J_{4x,5}$ is 1.61 Hz. This is in agreement with published data on other bicyclo[3.1.0] ring systems [13] which suggest that the *cis*-coupling should be *ca.* 6.5 Hz and much larger than the *trans*-coupling. (iii) Similarly, $J_{5,6}$ would be predicted [13] to be in the region of 4 Hz in the *exo*-isomer and *ca.* 8 Hz in the *endo*-isomer. As we find a value of 3.43 Hz, this is additional evidence for an *exo*-assignment.

TABLE 1

N.m.r. data for *exo*- and *endo*-compounds (5a) and (4a)

Chemical shifts (δ)

Proton	*exo* (5a)	*endo* (4a)
H-1	1.67	1.97
H-2	5.77	5.53
H-3	5.34	5.48
H-4*x*	2.16	2.04
H-4*n*	2.45	2.20
H-5	1.40	1.57
H-6	0.25	1.06
CH_2	2.79	2.64

Coupling constants (Hz)

J	*exo* (5a)	*endo* (4a)
1,2	2.07	2.2
1,3	0.34	<0.5
1,4*x*	2.83	2.2
1,4*n*	1.18	1.1
1,5	6.26	6.2
1,6	2.51	7.2
1,CH_2	0.31	<0.5
2,3	5.58	5.5
2,4*x*	2.17	2.2
2,4*n*	2.17	2.2
2,5	0.40	0.5
3,4*x*	2.20	2.2
3,4*n*	2.17	2.2
3,5	1.18	1.1
3,6	0.40	0.6
3,CH_2	~0	<0.5
4*x*,4*n*	17.79	18.4
4*x*,5	1.61	1.9
4*x*,6	0.56	0.9
4*x*,CH_2	0.30	~0
4*n*,5	6.60	7.8
4*n*,6	0.56	0.9
4*n*,CH_2	0.54	~0
5,6	3.43	7.6
5,CH_2	0.35	~0
6,CH_2	6.89	7.5
CH_2,NH	5.77	

The endo-*suphonamide* (4a). Unlike the *exo*-compound, the spectrum of the *endo*-compound shown in Figure 1(ii) has considerably smaller chemical shift differences at 90 MHz, the second-order nature of the nuclear spin system becomes evident and analysis of the coupling patterns is not possible by inspection. To aid the analysis, a spectrum has been measured at 400 MHz in [$^2H_6$]DMSO at 80 °C. Having made the assignments for the *exo*-compound, many of the shifts for the *endo*-isomer can be made by comparison.

Of the geminal pair at C-4, H-4*n* can be assigned to the low-field half on the basis of its coupling to H-5 as in the *exo*-compound and because, apart from the geminal coupling, H-4*x* has no other large coupling constants. H-1 and -5 can be distinguished by the number of coupling constants of *ca.* 6 Hz. H-1 is expected to couple to H-5 with a coupling constant of about this magnitude and although, *a priori*, the coupling to H-6 is not known, the coupling to H-2 is small. Hence a maximum of two 6 Hz couplings is expected for H-1. Since one band has three such couplings it cannot be H-1 and must therefore be H-5. The resonances due to H-2

and -3 can also be distinguished by comparing the observed coupling constants with those found for the *exo*-isomer (5a). Two bands, for H-1 and -3, could not be analysed by inspection even at 400 MHz but reasonable agreement with the observed bandshapes could be produced from the couplings taken from other bands, assuming a negligible value for $J_{1,3}$ as found for the *exo*-isomer. The coupling constant $J_{5,6}$ is found to be 7.6 Hz, again in agreement with the *endo*-stereochemistry [13] and in contrast to the value of 3.43 Hz found for the *exo*-isomer. All chemical shifts and coupling constants are summarised in Table 1.

Previous ^{1}H n.m.r. studies [7] on the *endo*-compound at 100 MHz in $CDCl_3$ solution using partially deuteriated material showed that the 7-methylene protons had non-equivalent chemical shifts, a feature which disappeared in [$^2H_6$]DMSO solution even at 400 MHz. The assignments obtained from the analysis of these two compounds allowed us to assign the spectra of other compounds in the series and these are summarised in Table 2. The chemical shift difference between the olefinic protons H-2 and -3 was always larger in the *exo*-series where distinct signals were always observed for each proton. Also H-6 in the *exo*-series always appeared upfield relative to the corresponding *endo*-compound (see Table 1).

For compounds of this type the ^{1}H n.m.r. spectral parameters obtained should be of value in aiding characterisation especially when the stereochemistry of the 6-substituents cannot be predicted from the mode of formation.

EXPERIMENTAL

^{1}H N.m.r. spectra were measured in the pulse-Fourier mode on a Bruker HFX-90 instrument with an Instem DATAMAG data processing system based on a PDP 11/15 computer. Spectra were obtained on solutions degassed by the passage of oxygen-free nitrogen.

Deuteriated solvents, $CDCl_3$ (99.7% D) and [$^2H_6$]DMSO (99.8% D), were purchased from Fluorochem Ltd., Glossop and used without further purification other than drying with molecular sieve. Spectra were measured at various temperatures up to 120 °C, control being maintained by a standard Bruker temperature-control unit. The full spectra shown in Figure 1 were obtained using a spectral width of 625 Hz and as the aromatic resonances lay outside this range they were allowed to fold into the frequency gap between the aliphatic and olefinic resonances and consequently are not shown. Each f.i.d. was acquired using single-phase detection into 8 192 data points and zero-filled to 16 384 before Fourier transformation. The resolution-enhanced spectra (Figure 2) were obtained by performing a Lorentzian–Gaussian transformation on the f.i.d. [14] before transformation. This f.i.d. was obtained from a solution in [$^2H_6$]DMSO, degassed, and measured at 100 °C.

Spin–lattice relaxation times, T_1, were measured using the (180°–τ–90°) inversion–recovery sequence at 60 °C on a degassed $CDCl_3$ solution. A period of 20 s was allowed between each acquisition in order to achieve essentially complete relaxation.

Nuclear Overhauser enhancement (n.O.e.) experiments were also performed in a pulse-Fourier transform mode in which the decoupler was switched on at the required frequency for 18.3 s at low power to avoid saturation of adjacent resonances, switched off, and a 90° pulse applied in order to acquire an f.i.d., the whole being repeated in order to build up to a suitable signal-to-noise ratio.

For the *endo*-compound (4a) a ^{1}H n.m.r. spectrum was measured at 80 °C on a degassed [$^2H_6$]DMSO solution at 400 MHz. Again Gaussian deconvolution [14] was applied to improve the spectral resolution.

M.p.s were determined using a Kofler hot-stage apparatus.

TABLE 2

^{1}H N.m.r. data of bicyclo[3.1.0]hex-2-enes. Chemical shifts (δ) and selected coupling constants (Hz)

Compd.	H-1	H-2	H-3	H-4*x*	H-4*n*	H-5	H-6	A	H-7	B	Others
(4a) [a]	1.97	5.53	5.48	2.04	2.20	1.57	1.06		2.64		
(4a)	1.8	5.33		1.9	2.42	1.54	1.04	2.80		2.53	Aromatics 7.78, 7.42
(4b)	*ca.* 1.8 [c]	5.33		1.9	2.42	1.54	1.04	2.80		2.53	*J*7A,7B ~12
(4c)	*ca.* 2.0 [c,d]	5.54		*ca.* 2.1 [c,d]	*ca.* 2.4 [c,d]	1.61	1.05	2.50		2.31	
(4d) [a]	1.99	5.63	5.55	2.07	2.40	1.60	1.08		3.17		OH 4.16
(4d)	*ca.* 2.1 [c]	5.59		2.09	2.52	1.70	1.22	3.49		3.34	*J*4*x*,4*n* 18.8
(4e)	*ca.* 2.1 [c]	5.59		2.09	2.52	1.72	1.22	3.49		3.34	*J*7A,7B 11.4
(4f)	*ca.* 2.1 [c]	5.59		2.09	2.52	1.72	1.22				*J*6,7A 7.0
(4g)	*ca.* 2.1 [c]	5.59		2.09	2.52	1.72		3.50		3.35	*J*6,7B 7.8
											*J*4*n*,5 ~8
											*J*5,6 ~7
(4h)	*ca.* 1.9 [c]	5.68		2.07	2.50	1.46			3.36		CH_3 1.13
(4i)	*ca.* 2.5 [c]	5.70		2.35	2.66	2.12			3.66		
(4j) [b]	*ca.* 2.4 [c]	5.84		*ca.* 2.3 [c]	2.72	1.97	1.42	3.96		3.90	*J*5,6 8.0, *J*6,7 10.3
(4k) [b]	*ca.* 2.4 [c]	5.84		*ca.* 2.3 [c]	2.72	1.97		3.96		3.90	$J_{4x,4n}$ ~18
(4l) [b]	*ca.* 2.4 [c]	5.84		*ca.* 2.3 [c]	2.72	1.97	1.42				
(5a) [a]	1.67	5.77	5.34	2.16	2.45	1.40	0.25		2.79		Aromatics 7.91, 7.56
(5b)	1.67	5.84	5.39	2.32	2.60	1.40	0.34		2.50		
(5c)	1.88	5.92	5.44	2.35	2.64	1.50	0.50	3.56		3.40	*J*4*x*,4*n* ~17
											$J_{6,7A}$ ~7
											*J*7A,7B ~10,
											$J_{6,7B}$ ~8
(5d) [b]	*ca.* 2.3 [c]	6.05	5.60	*ca.* 2.5 [c]	2.75	1.99	0.80		3.93		

$CDCl_3$ solvent unless otherwise stated. [a] [$^2H_6$]DMSO at 80 °C. [b] D_2O. [c] Chemical shifts can only be determined approximately because of overlapping signals. [d] Assignments of these chemical shifts can be interchanged.

I.r. Spectra were recorded using a Perkin-Elmer 237 instrument and for liquids relate to thin films. Routine ^1H n.m.r. spectra were determined for solutions in deuteriochloroform unless otherwise stated, using a Bruker HFX-90 or a Varian HA-100 spectrometer. Mass spectra (e.i.) were obtained, using Hitachi RMU6, A.E.I.MS9, or A.E.I.MS30 instruments, by Mr. A. Greenway. G.l.c. was performed by Mr. C. Simpson and his staff using Pye–Unicam 104/64 instruments and polycyanopropylmethylphenylmethylsiloxane OV-225 columns with a flow rate of 50 ml min^{-1} N_2. T.l.c. was performed using Merck Kieselgel GF254 in 0.25 mm layers for analytical work and 0.75 mm layers for preparative work. We thank Mr. P. R. W. Baker for microanalyses.

The following compounds were made by previously reported methods: *endo*-6-formylbicyclo[3.1.0]hex-2-ene (2; X = O) [5] and its hydrogen sulphite adduct (4j); [5] *N*-phenylsulphonyl-*endo*-6-aminomethylbicyclo[3.1.0]hex-2-ene (4a); [7] (7*RS*)-[7-$^2H_1$]-*N*-phenylsulphonyl-*endo*-6-aminomethylbicyclo[3.1.0]hex-2-ene (4b); [7] *endo*-6-aminomethylbicyclo[3.1.0]hex-2-ene (4c); [7] *endo*-6-hydroxymethylbicyclo[3.1.0]hex-2-ene (4d).[5]

endo-6-*Hydroxymethyl*-exo-6-*methylbicyclo*[3.1.0]*hex*-2-*ene* (4h).—Sodium borohydride (0.20 g) was added in portions over 15 min to a solution of *endo*-6-formyl-*exo*-6-methylbicyclo[3.1.0]hex-2-ene (7a) [9] (1.0 g) in methanol (15 ml) with stirring at 0 °C. The solution was stirred at room temperature for 2 h, the solvent was removed *in vacuo*, and the residue was diluted with water (20 ml). The resultant oil was extracted with ether, the extracts were dried (Na_2SO_4), and the solvent was removed *in vacuo* yielding an oil. Distillation (bath temperature 100 °C at 25 mmHg) gave the *alcohol* (0.85 g) as a mobile oil shown to be homogeneous by g.l.c. (Found: C, 77.7; H, 9.5. $C_8H_{12}O$ requires C, 77.4; H, 9.7%), ^1H n.m.r. data given in Table 2.

endo-6-*Hydroxymethyl*-exo-6-*chlorobicyclo*[3.1.0]*hex*-2-*ene* (4i).—Sodium borohydride reduction of *endo*-6-formyl-*exo*-6-chlorobicyclo[3.1.0]hex-2-ene (7b) [10] by the above procedure gave the alcohol (4i) as an unstable pale yellow oil, pure by t.l.c. (R_F 0.3, $CHCl_3$), $\nu_{max.}$ 3 300br (OH) cm^{-1}, ^1H n.m.r. data given in Table 2.

(7RS)-[7-$^2H_1$]-endo-6-*Hydroxymethylbicyclo*[3.1.0]*hex*-2-*ene* (4e).—The aldehyde (2; X = O) (1.0 g) in dry ether (10 ml) was added in portions over 15 min to a stirred slurry of [$^2H_4$]lithium aluminium hydride (0.25 g) in dry ether (15 ml). The reaction mixture was stirred at room temperature for 2 h and the excess of $LiAl^2H_4$ destroyed by careful addition of methanol and then water. The mixture was filtered and the filtrate evaporated. Distillation gave the alcohol (4e) (0.61 g) as a mobile oil, b.p. 84—86 °C at 10 mmHg, shown to be homogeneous by g.l.c. The ^1H n.m.r. spectrum showed the expected changes from that of the undeuteriated sample. The δ 3.34 and 3.49 absorptions now showed an integration for 1 H and appeared as doublets, *J* 8 and 7 Hz, respectively. Also the δ 1.22 absorption was now a quartet. Chemical shifts are given in Table 2.

[7-$^2H_2$]-endo-6-*Hydroxymethylbicyclo*[3.1.0]*hex*-2-*ene* (4f).—*endo*-Bicyclo[3.1.0]hex-2-ene-6-carboxylic acid [11] (1.0 g) in dry ether (10 ml) was added to a stirred slurry of [$^2H_4$]-lithium aluminium hydride (0.65 g) in dry ether (25 ml) at 20 °C. After heating the suspension under reflux for 14 h, the excess of reagent was destroyed by careful addition of water. The mixture was filtered, the filtrate washed with aqueous sodium carbonate, dried ($MgSO_4$), and the solvent removed *in vacuo*. Distillation gave the alcohol (0.7 g), b.p. 84—86 °C at 10 mmHg, which was homogeneous by g.l.c. The ^1H n.m.r. spectrum showed the expected changes from that of the undeuteriated sample. The δ 3.34 and 3.49 absorptions were now absent and the absorption at δ 1.22 was a triplet.

[6-$^2H_1$]-endo-6-*Formylbicyclo*[3.1.0]*hex*-2-*ene* (7c) *and its Hydrogen Sulphite Adduct* (4k).—A solution of the aldehyde (2; X = O) (2.0 g) in dioxan–deuterium oxide (50 ml; 3 : 2) containing sodium methoxide (75 mg) was allowed to stand at room temperature for 6 days in a stoppered flask. After this time the reaction mixture was poured on 0.1N-hydrochloric acid (25 ml) and extracted with ether. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo* leaving a tan oil. This was dissolved in methanol and treated with aqueous sodium metabisulphite to give the hydrogen sulphite adduct (4k) as a solid. The aldehyde (7c) was regenerated from the hydrogen sulphite adduct with aqueous sodium carbonate, isolated with ether, and distilled yielding an oil (0.50 g), b.p. 72—74 °C at 40 mmHg, shown to be homogeneous by g.l.c., $\nu_{max.}$ 1 695 and 1 614 cm^{-1}, δ for (7c) 2.28 (1 H, d, *J* 6 Hz, H-1), 2.68 (3 H, m, H-4 and -5), 5.82 (2 H, s, H-2 and -3), 9.14 (1 H, s, H-1), δ for (6c) 1.86 (2 H, t, *J* 2.2 Hz, H-8), 4.87br (1 H, s, H-1), 5.38 (1 H, dd, *J* 5.5 and 3.2 Hz, H-7), 5.80 (1 H, s, H-3), and 6.44 (1 H, dd, *J* 5.5 and 2.5 Hz, H-6), *m/e* 109 (M^+). From the intensities of the *m/e* 109 and 108 peaks, the incorporation was found to be 89% $^2H_1$, 11% $^2H_0$. The hydrogen sulphite adduct (4k) was prepared from the pure aldehyde (7c) as above, being obtained as a solid. The ^1H n.m.r. spectrum (D_2O) showed the expected changes from that of the undeuteriated sample. The δ 1.42 absorption was now almost absent and the δ 3.90 and 3.96 absorptions were now singlets.

[6-$^2H_1$]-endo-6-*Hydroxymethylbicyclo*[3.1.0]*hex*-2-*ene* (4g).—Sodium borohydride reduction of aldehyde (7c) was carried out as above yielding the alcohol (4g) as an oil, b.p. 84—86 °C at 10 mmHg, shown to be homogeneous by g.l.c. The ^1H n.m.r. spectrum showed the expected changes from that of the undeuteriated sample. The δ 1.22 absorption was now almost entirely absent and the absorptions at δ 3.35 and 3.50 now appeared as an AB quartet, *J* 12 and 11 Hz.

[7-$^2H_1$]-endo-6-*Formylbicyclo*[3.1.0]*hex*-2-*ene* (8b) *and its Hydrogen Sulphite Adduct* (4l).—7-*endo*-Chlorobicyclo[3.2.0]-hept-2-en-6-one [12] (9) (3.0 g) was added dropwise over 10 min to a stirred solution of [$^2H_4$]sodium borohydride (0.40 g) in deuterium oxide–[$^2H_1$]methanol (14 ml; 1 : 1), with external cooling to maintain the temperature at 20 °C. The mixture was stirred for 1 h, poured onto water, and extracted with chloroform. The extracts were dried (Na_2SO_4) and the solvent removed *in vacuo* yielding an oil (2.5 g). Aqueous 2N-sodium hydroxide (110 ml) was added and the mixture was shaken vigorously for 5 min and extracted with chloroform. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo*. Distillation yielded the deuteriated aldehyde (8b) (1.4 g) as an oil, b.p. 68—70 °C at 25 mmHg, which was shown to be homogeneous by g.l.c., *m/e* 109(M^+), $\nu_{max.}$ 2 095 (C–D) and 1 680 cm^{-1}. The ^1H n.m.r. spectrum showed the following expected changes from that of the undeuteriated aldehyde (2; X = O).[5] The doublets at δ 9.14 (H-7, aldehyde) and 5.88 (H-3, vinyl ether) were now absent. The δ 4.92 absorption (H-4, vinyl ether) was now a doublet, *J* 6 Hz. The δ 1.60 absorption [H-6 for (8b)] was now a triplet. The aldehyde (8b) was converted into its hydrogen sulphite adduct (4l) as above yielding a solid. The ^1H n.m.r. spectrum showed the expected changes from that of the undeuteriated sample. The δ 3.90 and 3.96 absorptions were now absent and the absorption at δ 1.42 now appeared as a triplet.

exo-6-*Formylbicyclo*[3.1.0]*hex*-2-*ene*[7] (3; X = O) *and its Hydrogen Sulphite Adduct* (5d).—A solution of the aldehyde (2; X = O) (10 g) in ethanol (50 ml) was added to a solution of sodium (0.4 g) in ethanol (70 ml) and the resulting solution was heated at reflux for 6 h under nitrogen. The solvent was removed *in vacuo* and the dark residue was distilled giving the product (4.8 g) as an oil, b.p. 70—72 °C at 20 mmHg. G.l.c. showed the presence of one major component (95%), *m/e* 108 (M^+), $\nu_{max.}$ 1 690 cm^{-1}, δ ($CDCl_3$) 1.26 (1 H, m, H-6), 2.35 and 2.5—2.9 (4 H, m, H-1 + -5 + -4), 5.56 (1 H, m, H-3), 5.92 (1 H, m, H-2), 9.25 (1 H, d, *J* 4.5 Hz, H-7). The aldehyde (3; X = O) was converted into the hydrogen sulphite adduct (5d) as above yielding a solid. ^1H N.m.r. data are given in Table 2.

exo-6-*Hydroxyiminobicyclo*[3.1.0]*hex*-2-*ene* (3; X = NOH).—Hydroxylamine hydrochloride (0.8 g) was added in portions over 10 min to a stirred suspension of the aldehyde (3; X = O) (1.0 g) in aqueous methanol (10 ml; 1 : 1) containing potassium carbonate (0.6 g). The mixture was stirred at room temperature for 2 h and extracted with chloroform. The extracts were dried ($MgSO_4$) and the solvent removed *in vacuo*. Sublimation (bath temperature 100 °C at 0.5 mmHg) gave the *oxime* (3; X = NOH) (0.75 g), m.p. 77—79 °C (Found: C, 68.5; H, 7.3; N, 11.3. C_7H_9NO requires C, 68.3; H, 7.4; N, 11.4%); δ ($CDCl_3$) 0.90 (1 H m, H-6), 1.66 (1 H, m, H-5), 1.87 (1 H, m, H-1), 2.22 (1 H, m, H-4*x*), 2.55 (1 H, m, H-4*n*, *J* 18, 6 Hz), 5.48 (1 H, m, H-3), 5.92 (1 H, m, H-2), and 6.04 and 7.03 (1 H, d, *J* 8 Hz, H-7*syn* and -7*anti*).

exo-6-*Aminomethybicyclo*[3.1.0]*hex*-2-*ene* (5b).—A solution of oxime (3; X = NOH) (0.4 g) in dry THF (10 ml) was added to a stirred slurry of lithium aluminium hydride (0.2 g) in dry ether (30 ml) over 20 min. The suspension was stirred at room temperature for 14 h and excess of reagent was destroyed by careful addition of water. After filtration, the solvent was removed *in vacuo*, the residue diluted with water, and extracted with chloroform. The extracts were dried (Na_2SO_4) and the solvent removed *in vacuo* to yield the amine (5b) (0.20 g) as an unstable yellow oil, R_F 0.1 ($CHCl_3$), $\nu_{max.}$ 3 300br (NH_2) cm^{-1}, ^1H n.m.r. data given in Table 2.

N-*Phenylsulphonyl*-exo-6-*aminomethylbicyclo*[3.1.0]*hex*-2-*ene* (5a).—The crude amine (5b) (0.20 g) was dissolved in anhydrous pyridine (6 ml) with benzenesulphonyl chloride (0.40 g). The solution was left at room temperature for 5 h, poured onto 2N-hydrochloric acid (20 ml), and extracted with chloroform. The extracts were dried (Na_2SO_4) and the solvent was removed *in vacuo*. Purification by preparative t.l.c. (R_F 0.2, $CHCl_3$), yielded the *sulphonamide* (5a) (0.21 g) as a fawn solid, m.p. 57—59 °C (Found: C, 62.8; H, 6.2; N, 5.5. $C_{13}H_{15}NO_2S$ requires C, 62.6; H, 6.1; N, 5.6%), ^1H n.m.r. data given in Tables 1 and 2.

exo-6-*Hydroxymethylbicyclo*[3.1.0]*hex*-2-*ene* (5c).—Sodium borohydride reduction of the *exo*-aldehyde (3; X = O) was carried out as above yielding the alcohol as a mobile oil, b.p. 88—91 °C at 20 mmHg, which was shown to be homogeneous by g.l.c. (Found: C, 76.5; H, 9.0. $C_7H_{10}O$ requires C, 76.35; H, 9.15%), ^1H n.m.r. data given in Table 2.

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