The Preparation from Cyclopentadiene Trimer of Alcohols and Ketones containing the Perhydro-4,9:5,8-dimethanobenz[*f*]indene Ring System

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endo,exo,endo-Perhydro-4,9:5,8-dimethanobenz[*f*]inden-6-*exo*-ol (2) and other alcohols and ketones containing the perhydro-4,9:5,8-dimethanobenz[*f*]indene ring system in either the *endo,exo,endo*- or the *exo,exo,endo*-form have been prepared from cyclopentadiene trimer (1). The acid-catalysed addition of water and various carboxylic acids to the 2,3-double bond of the diene (1) has been investigated. It appears that the degree of Wagner–Meerwein rearrangement accompanying such additions is related to the steric bulk of the addend. The route employed for the preparation of the bridgehead 3a-alcohol (26) involved the stereo- and regio-selective allylic oxidation of the 2,3-olefin (15) with t-butyl perbenzoate and a copper-salt catalyst. The mass and ^{13}C n.m.r. spectra of representative alcohols and ketones are reported.

In connection with studies in these laboratories of the microbiological hydroxylation of rigid, cyclic systems [1] we required various alcohols and ketones [*e.g.* (2), (7), *etc.*] containing the perhydro-4,9:5,8-dimethanobenz[*f*]-indene ring system.

Surprisingly, in view of its ready availability, there has been relatively little work carried out on cyclopentadiene trimer (1). Nevertheless, sufficient is known of its chemistry to indicate that it is a particularly suitable starting material for the preparation of the required compounds. For example, the two double bonds in structure (1) differ considerably in reactivity [2–4] thus making it possible to functionalise the molecule at either end or at both. Also, acid-catalysed additions to the 6,7-double bond proceed with Wagner–Meerwein rearrangement,[3–5] and thus the trimer (1) can be used for the preparation of compounds in both the *endo,exo,endo*- and the *exo,exo,endo*-series. Finally, since only one face of each double bond in (1) is relatively free from steric hindrance, the introduction of substituents in a stereospecific fashion should be readily accomplished.

Cyclopentadiene trimer (1) has been prepared previously by heating cyclopentadiene, or its dimer, in a sealed vessel.[6–9] We found, however, that it could be obtained more expeditiously by heating redistilled *endo*-cyclopentadiene dimer at 140—150 °C under reflux in nitrogen for 24 h. Under these conditions the yield of purified trimer (1) is small (*ca.* 6%), but unchanged dimer is easily recovered and recycled. The structure of cyclopentadiene trimer (1) formed from the *endo*-dimer has been fully elucidated by chemical methods and confirmed by a detailed analysis of its n.m.r. spectrum.[10,11]

The route chosen for the preparation of 6-oxygenated *endo,exo,endo*-compounds involved, as a first step, the treatment of the trimer (1) with mercury(II) acetate followed by sodium borohydride. The oxymercuration–demercuration reaction [12] of norbornene derivatives has been shown previously to proceed without Wagner–Meerwein rearrangement, and with a high degree of specificity on the *exo*-face.[13] Since the 6,7-double bond of cyclopentadiene trimer (1) is more reactive than the 2,3-double bond, and its *endo*-face is more hindered than that of the norbornene double bond, it was expected that oxymercuration–demercuration would proceed both regio- and stereo-specifically. In fact when the mixture of unsaturated acetates and alcohols initially obtained was hydrogenated over platinum and then hydrolysed, only one alcohol was isolated. The overall yield was high when 1 mol. equiv. of mercury(II) acetate was employed, but was lowered by the use of an excess of reagent. The structure (2) expected for the product was confirmed by its ^1H n.m.r. spectrum, which contains a broad doublet at τ 5.95 (J 6 Hz), typical of *endo*-α-protons.[14] Furthermore the substantial downfield shift of this signal as compared with the corresponding signal in norbornan-2-*exo*-ol [$\tau(CCl_4)$ 6.42] [14] indicates the presence of an *endo*-linkage at the 4a-position [*cf.* 6-*endo*-methylnorbornan-2-*exo*-ol which has the 2-proton resonance at $\tau(CCl_4)$ 5.99 (br d, J 7 Hz)[15]].

Oxidation of the alcohol (2) can be carried out with Jones reagent, but better yields of the ketone (3) were obtained when Brown's two-phase procedure was used.[16] An excess of reagent was required, and the reaction proceeded unusually slowly, presumably because of the severe steric hindrance to base-promoted removal of the α-proton in the intermediate chromate ester.[17] The

[1] A. L. J. Beckwith, M. Gilpin, and E. R. H. Jones, unpublished observations; F. Blaney, D. E. Johnson, M. A. McKervey, E. R. H. Jones, and J. Pragnell, *J.C.S. Chem. Comm.*, 1974, 297.
[2] K. Alder and G. Stein, *Annalen*, 1932, **496**, 204.
[3] H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, 1945, **67**, 723.
[4] F. Bergmann and H. Japhe, *J. Amer. Chem. Soc.*, 1947, **69**, 1826.
[5] H. A. Bruson, U.S.P. 2,395,452 (*Chem. Abs.*, 1946, **40**, 3138).
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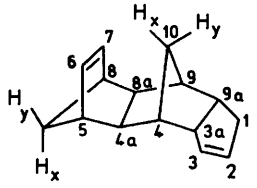
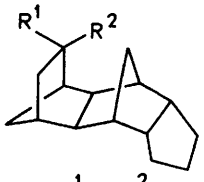
[7] K. Alder and G. Stein, *Annalen*, 1931, **485**, 223.
[8] K. Alder and G. Stein, *Angew. Chem.*, 1934, **47**, 837.
[9] B. Raistrick, R. H. Shapiro, and D. M. Newitt, *J. Chem. Soc.*, 1939, 1761.
[10] R. G. Foster and M. C. McIvor, *J. Chem. Soc.* (*B*), 1969, 188 and references cited therein.
[11] R. G. Foster and M. C. McIvor, *Org. Magnetic Resonance*, 1969, **1**, 203.
[12] H. C. Brown and P. J. Geoghegan, *J. Org. Chem.*, 1970, **35**, 1844.
[13] H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, 1967, **89**, 1525; P. Wilder, A. R. Portis, G. W. Wright, and J. M. Shepherd, *J. Org. Chem.*, 1974, **39**, 1636.
[14] A. Coulombeau and A. Rassat, *Bull. Soc. chim. France*, 1970, **12**, 4393.
[15] D. E. Gwynn and L. Skillern, *Chem. Comm.*, 1968, 490.
[16] H. C. Brown, C. P. Garg, and K. T. Liu, *J. Org. Chem.*, 1971, **36**, 387.
[17] H. O. House, 'Modern Synthetic Reactions,' 2nd edn., Benjamin, California, 1972, p. 261.

n.m.r. spectrum of the ketone (3) contains a signal from only one proton with a shift in the bridgehead region at τ *ca.* 8.8,[11] and this is assigned to H_y at the 10-position, since other bridgehead protons are expected to be deshielded by the carbonyl group.



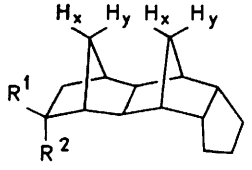
(1)



	R^1	R^2
(2)	OH	H
(3)	O	
(4)	H	OH
(5)	OAc	H
(6)	H	OAc

Reduction of the ketone (3) with sodium borohydride proceeded smoothly but slowly (see below) and unusually rigorous conditions were required. The sole product was different from the alcohol (2) and was therefore assigned the structure (4), further support for which is provided by the similarity of the n.m.r. signal of the α-proton (τ 5.73, broad m), to that of the equivalent proton in norbornan-2-*endo*-ol (τ 5.88, broad m).[14]

The reaction of formic acid with cyclopentadiene trimer (1) has been reported to proceed with Wagner–Meerwein rearrangement to afford an *exo,exo,endo*-monoadduct in quantitative yield.[4] However, when the trimer (1) was heated under reflux with formic acid for 8 h the product was shown by n.m.r. spectroscopy to contain *ca.* 17% of starting material. The reaction of the trimer (1) with formic acid in chloroform proceeded more cleanly and gave a quantitative yield of formates. However, the n.m.r. spectra of the products from both reactions contained resonances at τ 5.15 and 4.95 indicative of the presence of both *exo,exo,endo*- and *endo,exo,endo*-formates. This was confirmed by hydrogenation and hydrolysis of the mixtures of formates, which afforded mixtures of two alcohols. The n.m.r. spectra of the products contained two broad doublets in the α-proton region. The minor (*ca.* 20%) at τ 5.95 (J 6 Hz) corresponds to the signal for the α-proton in the unrearranged alcohol (2), and the major (*ca.* 80%) at τ 6.25 (J 7 Hz) is assigned to the required rearranged *exo*-alcohol (7).



	R^1	R^2
(7)	OH	H
(8)	O	
(9)	H	OH
(10)	OAc	H
(11)	H	OAc
(12)	H	OMe

The separation of the isomeric alcohols (2) and (7) proved difficult. Both column chromatography and t.l.c. with a variety of solvents and adsorbents were ineffective. Fractional crystallization from methanol or light petroleum gave crystalline samples, but they had differing m.p.s and their n.m.r. spectra showed them to be mixtures. One such sample, m.p. 104—106°, comprised a 2 : 1 mixture of (2) and (7); presumably the material of similar m.p., previously regarded as pure (7),[3] was also a mixture. Eventually a pure sample of the rearranged alcohol (7) was obtained by fractional crystallization of the mixture from nitromethane–methanol. An alternative method, suitable only for small quantities, involves preparative t.l.c. of a mixture of the acetates (6) and (10) followed by alkaline hydrolysis of the fraction of higher R_F value. As expected the signal for the α-proton appeared in the n.m.r. spectrum of (7) as a high-field doublet (τ 6.25, J 7 Hz).

In an attempt to develop a more specific route to the rearranged alcohol (7), the trimer (1) was treated with a number of different acids. In each case the crude product was hydrogenated, hydrolysed, where appropriate, with methanolic potassium hydroxide, and analysed by g.l.c. The results (Table 1) reveal some interesting trends.

First, as expected for a reaction believed to proceed by initial protonation of the diene (1), the rate is related to the strength of the acid. Among the carboxylic acids the order of reactivity is trifluoroacetic > trichloroacetic > formic > acetic; the reactions of acetic and isobutyric acids are extremely slow even at reflux temperature, and acceptable yields of products were obtained only when a strong mineral acid catalyst was added.

TABLE 1

Relative yield of rearranged product from acid-catalysed addition to cyclopentadiene trimer (1)[a]

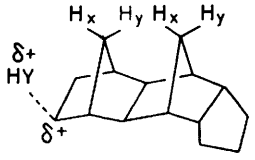
Addend	Catalyst	Solvent	Reaction time (h)	Temp. (°C)	Yield[b] (%)
Bu^tCO_2H (10 ml)	HBF_4 (0.5 ml)[c]		10	110	10
Pr^iCO_2H (10 ml)	HBF_4 (0.5 ml)		1	110	14
$Cl_3C{\cdot}CO_2H$ (1 g)		CCl_4 (12 ml)	5	80	36
$F_3C{\cdot}CO_2H$ (1 g)		CCl_4 (10 ml)	0.1	80	56
AcOH (10 ml)	HBF_4 (0.5 ml)		0.4	115	88
HCO_2H (3 ml)		$CHCl_3$ (7 ml)	24	*ca.* 65	82
HCO_2H (10 ml)			4	100	88
H_2O (2 ml)	HBF_4 (0.5 ml)	Dioxan (8 ml)	4	100	80
H_2O (2 ml)	H_2SO_4 (0.4 g)	Dioxan (8 ml)	2	100	84

[a] 0.4 g in each experiment. [b] As percentage of total yield of adducts. [c] 43% w/v in water.

The degree of rearrangement accompanying addition appears to be independent of the strength of the acid. It may be slightly dependent on the temperature; the results suggest that the formation of rearranged products is favoured by higher temperatures, but more closely controlled experiments are needed to confirm this. The extent of rearrangement appears to be determined mainly

by the bulk of the nucleophile. The small reagents water, formic acid, and acetic acid afford relatively high yields of rearranged products, but the bulky trichloroacetic and isobutyric acids give mainly unrearranged *endo,exo,endo*-compounds.

This observation of a relationship between the extent of rearrangement accompanying addition to a norbornene system and the size of the reagent appears to be without precedent. We believe that in this instance it reflects secondary steric effects involving non-bonded interactions between H_x on the 4,9-methano bridge and adjacent protons. The outcome of the attack of a nucleophile HY on a pair of rapidly equilibrating ions [18] (or on a non-classical norbornyl cation) will reflect the relative stability of the two transition states (13) and (14). When Y is small the dimensions of each transition



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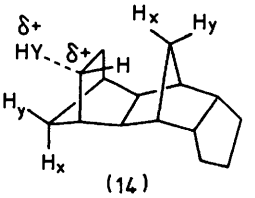


(14)

state should be very similar to those of the appropriate parent hydrocarbon, and we expect, therefore, that such reactions will proceed more readily through that structure (13) which contains the preferred *exo*-configuration at the 4a,8a-ring junction.

When HY is large there will be an interaction between Y and the adjacent proton at C-11. In the case of the transition state (14) this can be relieved by increase in the 11,5,6- and 11,8,7-bond angles, a perturbation which causes very little increase in the non-bonded interactions of 10-H_x with adjacent protons. However, in the case of transition state (13) any similar change in the 11,5,6- and 11,8,7-bond angles will cause a large increase in the steric interaction of the buttressed protons 11-H_y and 10-H_x. We conclude that when Y is large, the transition state (13) is destabilized with respect to (14) and that products will be formed preferentially *via* the latter.

The ketone (8) was obtained by Brown oxidation of the rearranged alcohol (7) or, more conveniently, of a mixture of the alcohols (2) and (7). In the latter case the resultant mixture of ketones (3) and (8) could be separated by chromatography. The ketone (3) so obtained was identical with the compound formed directly from the unrearranged alcohol (2). In agreement with the assigned structure the ketone (8) shows one high-field doublet in its n.m.r. spectrum, due to 10-H_y.

Reduction of the *exo,exo,endo*-ketone (8) with lithium aluminium hydride or sodium borohydride afforded a 9 : 1 mixture of the *endo*- (9) and the *exo*-alcohol (7), a product distribution typical of metal hydride reductions of unhindered norbornan-2-one-type compounds.[19] As expected the signal for the α-proton in the n.m.r. spectrum of the *endo*-alcohol (9) was a multiplet at lower field than that for the α-proton in the *exo*-isomer (7).

Qualitative studies indicated that there is a large difference between the rates of reduction of the ketones (8) and (3) with sodium borohydride, the former being the more reactive. Presumably, reduction of the *endo,exo,-endo*-ketone (3) is hindered by the increase in non-bonded interaction between the oxygen atom and 10-H_x as a tetrahedral centre develops at C-6. The difference in reactivities of the two ketones allows the reduction to be conducted selectively. When a mixture of (3) and (8) was treated with 1 mol. equiv. of sodium borohydride in ethanol at room temperature for 40 min the latter was completely reduced, but the former was virtually unaffected. The resultant mixture of the ketone (3) and the two alcohols (7) and (9) was readily separated by chromatography.

In an endeavour to develop a more stereospecific route to the alcohol (9), catalytic hydrogenation of the ketone (8) was attempted. However, reduction would not proceed until trifluoroacetic acid was added to the mixture, and the reaction then produced the epimeric alcohols (7) and (9), and a less polar compound, the properties of which agree with its formulation as the *endo*-6-methoxy-compound (12). This may have arisen *via* intermediate formation and subsequent hydrogenation of a methyl vinyl ether.

Alder and Stein [2] reported that the mono-ene (15) can be prepared by partial hydrogenation of the trimer (1). However, when the hydrogenation of (1) over platinum in methanol was stopped after absorption of 1 mol. equiv. of hydrogen, the product was found to contain appreciable quantities of both the diene (1) and the fully saturated compound (19). The use of palladium–charcoal as catalyst ensured a more selective reaction, but the best results were obtained when Brown's nickel boride [20] was employed.

Oxidation of the olefin (15) with selenium oxide in acetic acid gave, after hydrolysis and purification of the product over precipitated silver,[21] the allylic alcohol (16). The *exo*-stereochemistry is assigned on the ground that *endo*-attack would be subject to considerable steric hindrance, and is supported by the presence in the n.m.r. spectrum of the alcohol (16) of a sharp singlet at τ 5.30 assigned to the α-proton. The epimeric alcohol (18) would be expected to show considerable coupling between the α-proton and H-9a. Oxidation of the alcohol (16) with Jones reagent afforded the ketone (17) in modest yield.

Hydrogenation of the alcohol (16) without concomitant hydrogenolysis was accomplished with the use of rhodium –alumina, the catalyst of choice for reduction of allylic alcohols.[22] Oxidation of the alcohol (20) thus prepared, by the two-phase method, afforded the ketone (21) in

[18] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 1975, **97**, 5521; and references cited therein.

[19] H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, 1965, **87**, 5620.

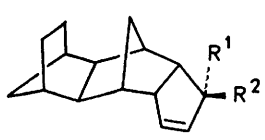
[20] H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, 1963, **85**, 1005.

[21] L. F. Fieser and G. Ourisson, *J. Amer. Chem. Soc.*, 1953, **75**, 4404.

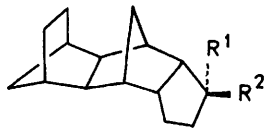
[22] H. O. House, 'Modern Synthetic Reactions,' 2nd edn., Benjamin, California, 1972, p. 13.

good yield. Its n.m.r. spectrum contains resonances in the high-field region (*ca.* τ 8.8) for five protons, the bridge protons at C-10 and C-11 accounting for four of these. The other resonance is assigned to H-8a, which is substantially shielded by the carbonyl group. Reduction of the ketone (21) with lithium aluminium hydride or sodium borohydride afforded solely the *endo*-alcohol (22).

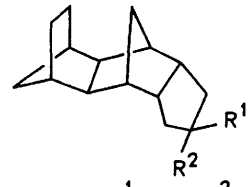
catalysed benzoyloxylation of olefins with t-butyl perbenzoate exhibits marked regio- and stereo-selectivity. The reaction is sensitive to steric hindrance, and proceeds preferentially by loss of tertiary hydrogen atoms to give products containing the less substituted possible double bond. It was expected therefore that the reaction of the olefin (15) with t-butyl perbenzoate would proceed *via*



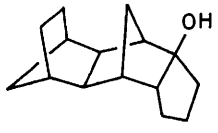
	R^1	R^2
(15)	H	H
(16)	H	OH
(17)	O	
(18)	OH	H



	R^1	R^2
(19)	H	H
(20)	H	OH
(21)	O	
(22)	OH	H



	R^1	R^2
(23)	OH	H
(24)	O	
(25)	H	OH



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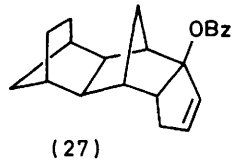

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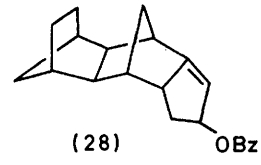

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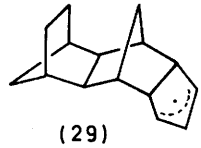

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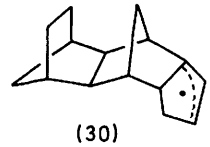

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As expected, the reaction of the olefin (15) with borabicyclononane occurred stereospecifically on the less hindered *exo*-face, but was not regioselective, for it produced, after oxidative work-up, a mixture of the two *exo*-alcohols (20) and (23). The mixture could not be separated chromatographically, but pure samples of the components were eventually isolated by fractional crystallization.

Brown oxidation of a mixture of the alcohols (20) and (23) afforded the readily separable ketones (21) and (24). In a later experiment the olefin (15) was treated with diborane and the product was oxidized directly with chromic acid. This procedure afforded not only the expected ketones (21) and (24), but also the saturated hydrocarbon (19); clearly under the conditions used protolysis of the intermediate borane competes with its oxidation.

Reduction of the ketone (24) with sodium borohydride proceeded rapidly and stereospecifically to afford the *endo*-alcohol (25).

For the preparation of the tertiary alcohol (26), use of the Kharasch reaction appeared to be practicable.[23] Recent investigations [23,24] have shown that copper-ion-

the allylic radicals (29) and (30), formed respectively by the loss of hydrogen atoms from the 1- and 3a-positions, with some preference for the latter. Selective conversion of the radical (30) into the tertiary benzoate (27) would then be aided both by the normal preference for formation of a disubstituted olefin, and by the considerable increase in ring strain engendered by formation of its trisubstituted isomer (28). In the event these expectations were realised. Heating the olefin (15) with t-butyl perbenzoate in the presence of copper(II) octanoate as catalyst gave a mixture of benzoates which was reduced with lithium aluminium hydride and hydrogenated over rhodium–alumina. G.l.c. showed the product to comprise mainly a mixture of the alcohols (20) and (26). Interestingly, the oxidation of the allylic radical (30) is completely regiospecific, for neither of the alcohols (23) or (25) was detected. Likewise, the oxidation of the alternative intermediate is highly stereospecific, for the product contained only a trace of the *endo*-alcohol (22). Treatment of the mixture of alcohols (20) and (26) with

[23] D. J. Rawlinson and G. Sosnovsky, *Synthesis*, 1972, 1.
[24] A. L. J. Beckwith and G. Phillipou, *Austral. J. Chem.*, 1976, **29**, 1277.

chromic acid under Brown's conditions smoothly oxidized the former; the pure alcohol (26) was readily separated chromatographically from the resultant mixture.

Mass Spectra.—All the saturated alcohols in the *endo,exo,endo*-series showed strong peaks at *m/e* 134 in their mass spectra, and for the 6-*exo*-, 1-*exo*-, and 1-*endo*-compounds [(2), (20), and (22)] this was the most abundant ion. In the case of the 6-hydroxy compounds (2) and (4), the ion *m/e* 134 appears to arise by loss of water from the molecular ion, followed by loss of C_5H_6 in a retro-Diels–Alder process. However, an appropriate metastable peak in the mass spectrum of the 1-*endo*-alcohol (22) indicates that in this case, at least, the molecular ion loses C_5H_8O in one step, and the same may be true of the other saturated 1- and 2-alcohols. Interestingly, the allylic alcohol (16) has a base peak at *m/e* 132. The formation of this ion must involve rearrangement, for there is no simple fragmentation pathway by which the molecular ion can lose C_5H_8O in either one step or two.

The two alcohols (7) and (9) in the *exo,exo,endo*-series behaved differently. In each case the most abundant ion had *m/e* 174. Although ions at *m/e* 200 formed by loss of water from the molecular ion were also detected, metastable defocusing experiments indicated that the ion at *m/e* 174 was formed in one step, presumably by loss of C_2H_4O in a retro-Diels–Alder process.

The mass spectra of the 6-ketones [(3) and (8)] were relatively simple, each showing an abundant molecular ion, and an important fragment ion at *m/e* 109, the formation of which must involve intramolecular hydrogen atom transfer to the oxygen atom followed by loss of C_8H_{11}. The mass spectra of the 1- and 2-ketones [(17), (21), and (24)] were more complex, each showing at least one abundant ion, *e.g.* with *m/e* 133, 83, and 105, respectively, the formation of which must involve rearrangements. However, in the case of each of the saturated ketones, (21) and (24), the ion at *m/e* 134 resulting from retro-Diels–Alder loss of C_5H_6O is also abundant.

TABLE 2

Chemical shifts [a] for ^{13}C nuclei in compounds containing the perhydro-4,9:5,8-dimethano-1*H*-benz[*f*]indene ring system

	(19)	(2)	(3)	(26)	(20)	(23)	(24)	(7)	(8)
C-1	26.5	26.5	26.6	25.7	74.3	35.8	39.1	26.4	26.3
C-2	29.4	29.3	29.4	29.2	38.5	76.1	220.3	29.5	29.5
C-3	26.5	26.5	26.1	36.3	24.0	35.8	39.1	26.4	26.3
C-3a	47.5	47.5	47.1	92.3	46.5	45.2	40.1	47.3	47.3
C-4	41.7	40.9	41.3	49.2	41.7	40.7	41.3	45.1	45.2
C-4a	42.3	40.4	40.2	41.5	43.2	42.2	41.1	39.7	40.1
C-5	41.4	50.3	56.1	41.3	41.5	41.5	41.3	48.6	54.2
C-6	24.7	71.0	219.2	24.7	24.6	24.6	24.7	75.4	216.7
C-7	24.7	38.2	42.6	24.7	24.6	24.6	24.7	44.25	48.4
C-8	41.4	40.7	39.3	41.3	41.5	41.5	41.3	41.1	40.5
C-8a	42.3	42.0	45.9	41.8	41.7	42.2	41.1	45.1	44.9
C-9	41.7	41.5	42.0	41.5	39.9	40.7	41.3	45.1	45.9
C-9a	47.5	47.5	47.0	58.3	57.7	45.2	40.1	47.5	47.3
C-10	39.1	39.6	39.6	36.5	38.4	37.8	36.9	40.3	39.2
C-11	42.3	38.4	39.9	42.8	42.6	42.5	42.0	32.7	35.4

[a] δ_C (p.p.m. from Me_4Si).

TABLE 3

Shielding effects (p.p.m.) of substituents on ^{13}C resonances for *endo,exo,endo*-perhydro-4,9:5,8-dimethano-1*H*-benz[*f*]indene

Position	1-*exo*-OH	2-*exo*-OH	3a-OH	6-*exo*-OH	2-Ketone	6-Ketone
C-1	+47.8	+9.3	−0.8	0.0	+12.6	+0.1
C-2	+9.1	+46.7	−0.2	−0.1	+190.9	0.0
C-3	−2.5	+9.3	+9.8	0.0	+12.6	−0.4
C-3a	−1.0	−2.3	+44.8	0.0	−7.4	−0.4
C-4	0.0	−1.0	+7.5	−0.8	−0.4	−0.4
C-4a	+0.9	−0.1	−0.8	−1.9	−1.2	−2.1
C-5	+0.1	+0.1	−0.1	+8.9	−0.1	+14.7
C-6	−0.1	−0.1	0.0	+46.3	0.0	+194.5
C-7	−0.1	−0.1	0.0	+13.5	0.0	+17.9
C-8	+0.1	+0.1	−0.1	−0.7	−0.1	−2.1
C-8a	−0.6	−0.1	−0.5	−0.3	−1.2	+3.6
C-9	−1.8	−1.0	−0.2	−0.2	−0.4	+0.3
C-9a	+10.2	−2.3	+10.8	0.0	−7.4	−0.5
C-10	−0.7	−1.3	−2.6	+0.5	−2.2	+0.5
C-11	+0.3	+0.2	+0.5	−3.9	−0.3	−2.4

^{13}C *N.m.r. Spectra.*—Off-resonance and broad-band decoupled ^{13}C n.m.r. spectra were recorded for the hydrocarbon (19), a number of its oxygenated derivatives, and the alcohol (7) and ketone (8) in the *exo,exo,endo*-series. Assignments (Table 2) were made by comparison between the spectra of closely related compounds, and by reference to previous work with norbornane derivatives.[25,26]

For example, the spectra of the hydrocarbon (19) and its derivatives containing oxygen functions at the 1-, 2-, or 3a-position each show a triplet resonance equivalent

[25] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, 1972.

[26] J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107.

to two carbon atoms close to δ 24.7, which is absent, however, from the spectra of the 6-oxygenated compounds (2) and (3). Clearly, this signal arises from C-6 and -7. Similarly, all the compounds studied which contained no substituent in the 1-, 2-, or 3a-position show a two-carbon triplet at *ca.* δ 26.5, and a less intense triplet at *ca.* δ 29.4. These must be assigned to C-1 and -3 and C-2, respectively.

Assignments for carbon atoms close to the position of functionality were made by comparison of the spectra with those of derivatives of 2-*exo*-hydroxy- and 2-oxo-norbornane.[26,27] Thus the chemical shifts for C-5, -6, and -7 are close to those reported for the equivalent positions in 6-*exo*-methylnorbornan-2-one.[27] Other assignments were made by trial and error. It is believed that those given in Table 2 for compounds in the *endo,-exo,endo*-series are unequivocal. However, since the parent hydrocarbon was unavailable, some of the assignments for the compounds (7) and (8) in the *exo,exo,endo*-series are less certain.

In Table 3 are given shielding effects for hydroxy-substituents at various positions in the *endo,exo,endo*-ring system. They agree well with those recorded previously for norbornanes and other cyclic systems. Since there is every indication that the normal additivity rules hold for compounds of the general type studied here, we expect that the data in Tables 2 and 3 will be of value for the determination of the structures of microbiological hydroxylation products.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded with a Unicam SP 1000 or a Perkin-Elmer 237 instrument for solutions in carbon tetrachloride, unless otherwise stated, and u.v. spectra with a Carey 14M spectrophotometer for ethanolic solutions. ^{1}H N.m.r. spectra were recorded with a Perkin-Elmer R-14 (100 MHz) or R-32 (90 MHz) instrument for solutions in carbon tetrachloride, unless otherwise stated. ^{13}C N.m.r. spectra were recorded for solutions in $CDCl_3$ with a Bruker WH 90 Pulse Fourier Transform instrument operating at 22.6 MHz. Sweep widths of 5—6000 Hz were used, giving an accuracy of *ca.* 0.1 p.p.m. to the figures quoted for the broad-band and off-resonance decoupled spectra. Mass spectra were recorded on a Varian MAT CH-7 (low resolution) or A.E.I. MS9 (high resolution) spectrometer. Microanalyses were carried out under the supervision of Dr. F. B. Strauss of these laboratories.

The silica gel used in column chromatography was of grade M60, and preparative layer chromatography was carried out with either large (20 × 100 cm) or small plates (20 × 20 cm) coated with 0.1 cm thickness of unbaked kieselgel $PF_{254:366}$. The maximum amount of material per small plate was 100 mg and per large plate 500 mg, but frequently much lower loadings were used. T.l.c. was performed on 20 × 5 cm plates coated with 0.1 mm of the above material. G.l.c. was conducted with a Perkin-Elmer 881 instrument [carrier gas (N_2) flow rate 30 ml min^{-1}]. On a 20 ft × $\frac{1}{8}$ in column of 3% PDEAS on Chromosorb W at 200 °C alcohols were eluted in the order (26), (25), (22), (7), (20), (2), (23) with retention times 11.8, 13.35, 14.65, 15.8, 16.6, 17.3, and 17.6 min, respectively. Ketones were separated on a 10 ft × $\frac{1}{8}$ in column of 5% Apiezon on Chromosorb W. At 220 °C the ketones (8) and (3) had retention times 18.2 and 19.6 min, respectively.

endo,exo,endo-3a,4,4a,5,8,8a,9,9a-*Octahydro*-4,9:5,8-*dimethano*-1H-*benz*[f]*indene* (1).—Cyclopentadiene dimer (250 ml; freshly purified by fractional distillation under reduced pressure) was heated in nitrogen under reflux, in an oil bath at 140—160 °C for 20 h. Distillation then afforded starting material, b.p. 68° at 15 mmHg, and a fraction (29 g), b.p. 125—140° at 10 mmHg, which solidified on cooling. The latter was triturated with cold ethanol (120 ml) and the resulting mixture filtered. Crystallization of the residue from methanol afforded the diene (1) (15.6 g), m.p. 66—67° (lit.,[1] 68°) (Found: C, 90.8; H, 9.2. Calc. for $C_{15}H_{18}$: C, 90.9; H, 9.1%), $\nu_{max.}$ 3060, 2970, 1667, 1615, 750, and 690 cm^{-1}, τ 4.09 (2 H, m, 6- and 7-H), 4.39 and 4.55 (2 H, 2m, 2- and 3-H), 7.05 (1 H, m, 3a-H), 7.28 (2 H, s, 5- and 8-H), 7.70—7.90 (4 H, complex), 8.00—8.10 (4 H, complex), 8.81 (2 H, m, 11-H), and 9.25 (1 H, d, *J* 10 Hz, 10-H$_y$), *m/e* 198 (M$^+$, 10%), 132 (21), 91 (14), 67 (19), 66 (100), and 65 (11). Less pure material (2.8 g), m.p. 60—64°, was obtained from the mother liquor.

endo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-6-exo-*ol* (2).—Mercury(II) acetate (3.3 g) in water (10 ml) was added with stirring during 10 min to cyclopentadiene trimer (1) (2.0 g) in tetrahydrofuran (20 ml) and water (3 ml) maintained at 20 °C. After further stirring (30 min) the suspension was treated with sodium borohydride (240 mg) in sodium hydroxide solution (3M; 10 ml). Ether (150 ml) was then added, and the mixture was filtered through Celite. The filtrate was washed repeatedly with water and with sodium hydrogen carbonate solution, dried, and evaporated to afford an oil (2.75 g), $\nu_{max.}$ 3610 and 1720 cm^{-1}, which was dissolved in methanol (60 ml) and hydrogenated (1 atm; 20 min) at room temperature over platinum oxide (60 mg). The mixture was then filtered through Celite and the filtrate was treated with potassium hydroxide (2 g) in water (3 ml), and heated under reflux for 1.5 h. After being concentrated under reduced pressure the mixture was diluted with water and extracted with ether. The ether layer was then washed and evaporated to afford the *alcohol*, which crystallised from cyclohexane in laths (2.0 g, 92%), m.p. 135—137° (Found: C, 82.5; H, 10.4. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%), $\nu_{max.}$ 3620, 1080, 1045, and 992 cm^{-1}, τ 5.95 br (1 H, d, *J* 6 Hz, 6-H), 7.60—8.20 (8 H, complex, 4-, 9-, 5-, 8-, 4a-, 8a-, 3a-, and 9a-H), 8.34—8.67 (9 H, complex, 1-, 2-, 3-, and 7-H and OH), and 8.77 and 8.90 (4 H, 2 m, 10- and 11-H), *m/e* 218 (8$^+$, 26%), 200 (70), 149 (35), 134 (100), 132 (79), and 66 (94).

The *acetate* (5), prepared by treatment with acetic anhydride–pyridine at ambient temperature overnight, crystallized from light petroleum in prisms, m.p. 61—62° (Found: C, 78.4; H, 9.3. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.2%), $\nu_{max.}$ 1735, 1370, 1250br, and 1035 cm^{-1}, τ 5.08 (1 H, d, *J* 6 Hz, 6-H), 7.5—8.25 (8 H, complex, 4-, 9-, 5-, 8-, 4a-, 8a-, 3a-, and 9a-H), 8.05 (3 H, s, Ac), 8.3—8.6 (8 H, complex, 1-, 2-, 3-, and 7-H), and 8.72 and 8.82 (4 H, 2 m, 10- and 11-H).

endo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-6-*one* (3).—An aqueous solution (25.0 ml) of chromic acid was prepared from sodium dichromate dihydrate (5.0 g) and concentrated sulphuric acid (3.75 ml). A sample (1.50 ml) was added slowly with stirring to the 6-*exo*-alcohol (0.44 g) in ether (15 ml) and the mixture was then stirred for a further 2 h. Ether and water were then added, and the ether layer, after being washed successively with dilute

[27] K. Alder and G. Stein, *Annalen*, 1933, **504**, 205.

sulphuric acid, water, and aqueous sodium carbonate, was dried and evaporated. Crystallization of the residue from light petroleum gave the *ketone* as prisms (0.33 g, 76%), m.p. 94—95° (Found: C, 83.35; H, 9.15. $C_{15}H_{22}O$ requires C, 83.3; H, 9.3%), $\nu_{max.}$ 1745, 1170, 1149, and 968 cm^{-1}, τ 7.36 (1 H, m, 5-H), 8.08 and 8.27 (2 H, 2 d, J 5 Hz), 8.45—8.6 (8 H, complex, 1-, 2-, 3-, and 11-H), and 8.78 (1 H, d, J 11 Hz, 10-H_y), *m/e* 216 (M^+, 98%), 173 (10), 133 (15), 109 (100), 91 (34), 79 (37), and 55 (*m**, 216 ⟶ 109).

endo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-6-endo-*ol* (4).—A solution of the ketone (3) (0.34 g) and sodium borohydride (0.12 g) in ethanol (10 ml) was boiled under reflux for 2.5 h, then cooled, diluted with water, and acidified. Extraction with ether afforded the *alcohol*, which crystallised from hexane in needles (0.27 g, 78%), m.p. 122—123° (Found: C, 82.4; H, 10.2. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%), $\nu_{max.}$ 3640, 1140, 1045, and 1015 cm^{-1}, τ 5.73 (1 H, partially resolved m of 6 lines, $W_{\frac{1}{2}}$ 20 Hz, 6-H), 7.4—8.05 (8 H, complex, 4-, 9-, 5-, 8-, 3a-, 9a-, 4a-, and 8a-H), 8.25—8.40 (2 H, m, 7-H), 8.42 and 8.52 (7 H, 2 m, 1-, 2-, and 3-H and OH), and 8.72 (4 H, m, 10- and 11-H), *m/e* 218 (M^+, 17%), 200 (26), 183.5 (*m**, 218 ⟶ 200), 149 (26), 134 (50), 132 (59), 89.5 (*m**, 200 ⟶ 134), and 66 (100).

The *acetate* (6) crystallised from light petroleum in needles, m.p. 88—89° (Found: C, 78.4; H, 9.3. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.3%), $\nu_{max.}$ 1740, 1235, and 1045 cm^{-1}, τ 5.15 (1 H, quint, J 5 Hz, 6-H), 7.5—8.15 (8 H, complex, 4-, 9-, 5-, 8-, 3a-, 9a-, 4a-, and 8a-H), 8.05 (3 H, s, Ac), 8.1—8.4 (2 H, m, 7-H), 8.56 (6 H, m, 1-, 2-, and 3-H), and 8.70 and 8.85 (4 H, 2 m, 10- and 11-H).

exo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-6-exo-*ol* (7).—A mixture of cyclopentadiene trimer (1) (3.0 g), formic acid (20 ml), and chloroform (40 ml) was boiled under reflux for 24 h, then cooled, diluted with ether, and shaken with water. After being washed with aqueous sodium carbonate the organic layer was evaporated to yield a mixture of formates as an oil (3.8 g), $\nu_{max.}$ 1725 and 1175 cm^{-1}, τ 2.05 (1 H, s, CHO), 4.95 (0.2 H, m, 6-H in *endo,exo,endo*-formate), and 5.15 (0.8 H, m, 6-H in *exo,exo,endo*-formate). A similar but less pure oil containing *ca.* 17% of starting material was obtained when cyclopentadiene trimer (4.0 g) in formic acid (2.8 g) was boiled under reflux for 8 h, and the product was then dissolved in ether and worked up as described above.

The oil (3.8 g) in methanol (60 ml) was hydrogenated (1 atm; 20 min) at ambient temperature over platinum oxide (60 mg). The resulting suspension was filtered, through Celite, and the filtrate was treated with potassium hydroxide (3.0 g) in water (6 ml) and refluxed for 2 h. Evaporation followed by partitioning of the residue between ether and water gave, on evaporation of the ether layer, a crystalline mixture of alcohols (3.0 g, 92%), estimated by n.m.r. to contain *ca.* 20% of the *endo,exo,endo*-compound (2) and *ca.* 80% of its isomer (7).

A sample (1.3 g) of the mixture was dissolved in nitromethane (20 ml) and methanol (5 ml), and the solution was set aside in an open flask at ambient temperature. The first crop of crystals (0.6 g), collected after 24 h, comprised a mixture of the two alcohols in approximately equal proportions. When the filtrate was set aside for a further 48 h there was obtained a second crop (0.45 g), m.p. 76—84°, which, when recrystallised from light petroleum, afforded the pure *alcohol* as laths, m.p. 88—90° (Found: C, 82.4; H, 10.2. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%), $\nu_{max.}$ 3630, 1070, 997, and 988 cm^{-1}, τ 6.25 (1 H, d, J 7 Hz, 6-H), 7.72 (2 H, m), 7.8—8.2 (6 H, complex), 8.2—8.8 (11 H, complex), and 8.84 (2 H, d, J 11 Hz, 10-H_y and 11-H_x); *m/e* 218 (M^+, 8%), 200 (46), 174 (100), 138.9 (*m**, 218 ⟶ 174), 107 (51), 91 (46), 66 (50), and 47.6 (*m**, 174 ⟶ 91).

Treatment of a sample (1.4 g) of the mixture of alcohols with pyridine (6 ml) and acetic anhydride (3 ml) at 80 °C for 1 h in the usual way afforded a mixture of acetates as an oil (1.8 g), which was applied to five preparative chromatography plates (1 m). Five elutions of the plates with 1 : 8 dichloromethane–light petroleum (b.p. 40—60 °C) gave partial separation, and allowed isolation of the exo,exo,endo-*acetate* (10) as an oil (Found: C, 78.5; H, 9.3. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.3%), $\nu_{max.}$ 1740, 1240, 1055, 1020, and 985 cm^{-1}, τ 5.45 (1 H, d, J 7 Hz, 6-H), 7.68 (2 H, m), 7.8—8.2 (6 H, complex), 8.00 (3 H, s, Ac), 8.2—8.65 (9 H, complex), 8.76 and 8.82 (3 H, 2 d, J 11 Hz, 10-H_x and -H_y and 11-H_x).

When a sample (600 mg) of the acetate was boiled under reflux with potassium hydroxide (1 g) in methanol (15 ml) and water (2 ml), the pure alcohol (480 mg) was obtained.

Addition of Acids to Cyclopentadiene Trimer.—Cyclopentadiene trimer and the acid were heated in the specified solvent until all the diene was consumed (t.l.c.). The mixture was then diluted with ether, and shaken with sodium carbonate solution and with water. The dried solution was evaporated and the residue, where appropriate, was heated with an excess of potassium hydroxide in aqueous ethanol until hydrolysis of esters was complete (t.l.c.). After the usual work-up the product was hydrogenated in methanol over platinum oxide and the product was analysed by g.l.c. The results are given in Table 1.

exo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-6-*one* (8).—A sample (3.6 g) of the mixture of alcohols obtained *via* treatment of cyclopentadiene trimer with formic acid was stirred in ether (50 ml) at 20 °C while acidified 2N-sodium dichromate (15 ml) was added dropwise during 10 min. The mixture was stirred for a further 1.5 h, then diluted with water and worked up in the usual way. Chromatography of the crude product (3.5 g) on alumina in ether–light petroleum afforded, from the first fractions, the *ketone* (1.4 g), which crystallized from light petroleum as prisms, m.p. 63—64° (Found: C, 83.0; H, 9.3. $C_{15}H_{20}O$ requires C, 83.3; H, 9.3%), $\nu_{max.}$ 1746, 1168, 1140, and 955 cm^{-1}, τ 7.6—8.1 (10 H, complex, 4-, 9-, 5-, 8-, 4-, 8a-, 3a-, 9a-, and 7-H), 8.16 (2 H, m, 10-H_x, and 11-H_y), 8.5—8.6 (7 H, complex), and 8.76 (1 H, d, J 10 Hz, 10-H_y), *m/e* 216 (M^+, 100%), 173 (13), 109 (45), 91 (21), 79 (27), 66 (15), and 55 (*m**, 216 ⟶ 109). Later fractions contained mixtures of the ketones (8) and (3). Smaller quantities of the mixture of ketones can be quantitatively separated by preparative t.l.c. with dichloromethane–light petroleum as solvent.

exo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-6-endo-*ol* (9).—(a) *From the ketone* (8). The ketone (0.80 g) was stirred in ether (10 ml) with an excess of lithium aluminium hydride at ambient temperature for 1 h. The usual work-up gave a solid which was chromatographed on plates with ether–hexane (1 : 9) as solvent. The less polar material, on crystallization from hexane, gave the endo-*alcohol* (0.67 g, 81%) as needles, m.p. 94—95°, or prisms, m.p. 123—124° (Found: C, 82.7; H, 10.1. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%), $\nu_{max.}$ 3640, 1220 br, 1115, 1075, 1053, and 1010 br cm^{-1}, τ 5.92 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, 6-H), 7.5—8.1 (10 H, complex), 8.2—8.45 (8 H, complex, 1-, 2-, 3-, and 7-H), 8.50 (1 H, s, D_2O exch., OH), 8.82 (1 H, d, J 11 Hz, 10-H_y), and 9.04 (1 H, d, J 11 Hz, 11-H_x), *m/e* 218 (M^+, 7%),

200 (29), 174 (100), 107 (58), 91 (53), and 66 (41). The *acetate* crystallised from light petroleum as needles, m.p. 36—37° (Found: C, 78.4; H, 9.5. $C_{17}H_{24}O_2$ requires C, 78.4; H, 7.3%), $\nu_{max.}$ 1740, 1240, 1120, 1050, and 1030 cm^{-1}, τ 5.25 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, 6-H), 7.5—8.1 (10 H, complex), 7.95 (3 H, s, Ac), 8.2—8.6 (8 H, complex, 1-, 2-, 3-, and 7-H), 8.80 (1 H, d, J 11 Hz, 10-H_y), and 8.95 (1 H, d, J 11 Hz, 11-H_x).

The more polar material from preparative t.l.c., on crystallization from light petroleum, gave the *exo*-alcohol (7) (37 mg).

(b) *From a mixture of the ketones* (8) *and* (3). A preliminary experiment to determine the relative rates of reduction of the ketones (8) and (3) was conducted as follows. A sample (20 mg) of the pure *exo,exo,endo*-ketone (8) was dissolved in ethanol (1.0 ml), and to it was added 1.0 ml of a solution of sodium borohydride (25 mg) in ethanol (2.5 ml). At the same time an otherwise identical mixture containing the *endo,exo,endo*-ketone (20 mg) was prepared. Both mixtures were set aside in a bath at 22 °C and the reaction was followed by t.l.c. After 20 min the *exo,exo,endo*-compound (8) was completely reduced, but the *endo,exo,endo*-isomer (3) showed only a faint spot for the reduction product. Complete reduction of the latter ketone required 24 h.

Accordingly, a sample (1.35 g) of a mixture of isomeric ketones estimated to contain 60% of the *exo,exo,endo*-compound was stirred in ethanol (30 ml) at 20 °C while sodium borohydride (70 mg) was added in small quantities during 5 min. The mixture was stirred for a further 40 min, then worked up in the usual way to afford an oily product (1.41 g), which was chromatographed on plates with dichloromethane–hexane (1 : 1) as solvent. The fraction (540 mg) of highest R_F value comprised the *endo,exo,endo*-ketone (3), the fraction (550 mg) of medium R_F was identified as the 6-*endo*-alcohol (9), and the 6-*exo*-alcohol (7) was obtained from the fraction (70 mg) of lowest R_F.

Catalytic Hydrogenation of the Ketone (8).—The ketone (300 mg) in methanol (20 ml) and trifluoroacetic acid (1 ml) was hydrogenated over platinum oxide. When uptake was complete (24 h) the mixture was filtered and evaporated. The residue, when chromatographed on a plate, afforded the *endo*-alcohol (9) (170 mg, 56%), the *exo*-alcohol (7) (20 mg, 6%), and an oil tentatively identified as the 6-*endo*-methoxy-compound (12) (80 mg, 23%), $\nu_{max.}$ 1450, 1210, 1120, 1100, and 1080 cm^{-1}, τ 6.45 (1 H, m, 6-H), 6.75 (3 H, s, OCH_3), 7.5—8.1 (10 H, complex), 8.2—8.6 (8 H, complex, 1-, 2-, 3-, and 7-H), 8.85 (1 H, d, J 11 Hz, 10-H_y), and 9.06 (1 H, d, J 11 Hz, 11-H_x), *m/e* 232 (M^+, <1%), 200 (100), 132 (20), 131 (21), 117 (22), 105 (24), 94 (45), 93 (58), 92 (77), 91 (42), 79 (57), 66 (58), and 67 (58).

endo,exo,endo-3a,4,4a,5,6,7,8,8a,9,9a-*Decahydro*-4,9:5,8-*dimethano*-1H-*benz*[f]*indene* (15).—A de-aerated solution of nickel acetate tetrahydrate (360 mg) in ethanol (12 ml, 96%) was stirred under nitrogen while a solution of sodium borohydride (65 mg) in ethanol was slowly added. Hydrogen (*ca.* 110 ml) was evolved, and a fine black precipitate was formed. Cyclopentadiene trimer (1) (1.50 g) in ethanol (20 ml) was then added, and the mixture was stirred under hydrogen. The uptake was initially rapid (*ca.* 10 ml min^{-1}) but became slower, and when 175 ml had been absorbed the rate was *ca.* 1.5 ml min^{-1}. When 1 mol. equiv. (185 ml) had been taken up, the mixture was degassed, then evaporated *in vacuo*. The residue was dissolved in light petroleum; the solution was filtered and evaporated to afford the olefin (1.48 g), which solidified to give needles, m.p. 38° (lit.,[2] 36°), $\nu_{max.}$ 3060, 2970, and 1615 cm^{-1}, τ 4.40 and 4.55 (2 H, 2m, 2- and 3-H), 7.05 (1 H, m, 3a-H), 7.4—8.0 (7 H, complex), 8.30 (2 H, m), 8.55—8.65 (4 H, complex, 6- and 7-H), and 8.80—8.95 (4 H, complex, 10- and 11-H), *m/e* 200 (M^+, 4%), 133 (50), 132 (85), 91 (41), 67 (54), and 66 (100).

endo,exo,endo-3a,4,4a,5,6,7,8,8a,9,9a-*Decahydro*-4,9:5,8-*dimethano*-1H-*benz*[f]*inden*-1-exo-*ol* (16).—The olefin (15) (7.42 g) in acetic acid (25 ml) and water (1 ml) was treated with selenium dioxide (4.55 g) and the mixture was stirred at 40 °C for 2 h. Ether was then added, and the solution was washed with saturated aqueous sodium hydrogen carbonate. The ethereal solution was filtered through Celite, and evaporated. The residual oily mixture of acetates and alcohols was refluxed with dioxan (100 ml) and 10% sodium hydroxide (100 ml). The mixture was concentrated *in vacuo* and the residue was taken up in ether; the solution was refluxed for 1 h over precipitated silver, and filtered. Evaporation of the filtrate gave the alcohol which crystallised from ethyl acetate–light petroleum in plates (6.53 g, 82%), m.p. 127—130°. Recrystallization gave a sample with m.p. 129—130° (with sublimation) (lit.,[27] 135°), $\nu_{max.}$ 3620, 3440br, 1611, 1001, and 965 cm^{-1}, τ 4.18 (2 H, m, 2- and 3-H), 5.30 (1 H, s, $W_{\frac{1}{2}}$ 6 Hz, 1-H), 6.82 (1 H, m, 3a-H), 7.73—7.86 (6 H, complex), 8.12 (1 H, d, J 10 Hz), 8.53—8.66 (5 H, complex), and 8.76—8.87 (4 H, complex, 10- and 11-H), *m/e* 216 (M^+, 12%), 132 (100), 106 (43), 104 (65), 82 (66), and 66 (66).

endo,exo,endo-3a,4,4a,5,6,7,8,8a,9,9a-*Decahydro*-4,9:5,8-*dimethano*-1H-*benz*[f]*inden*-1-*one* (17).—Oxidation of the alcohol (16) (1.00 g) by the Jones procedure, gave, after the usual work-up, the ketone (17), which crystallized from acetone–hexane as plates (550 mg, 56%), m.p. 160—162° (lit.,[27] 162°) (Found: C, 83.8; H, 8.3. Calc. for $C_{15}H_{18}O$: C, 84.1; H, 8.4%), $\nu_{max.}$ 1712, 1180, 1095, 920, and 890 cm^{-1}, $\lambda_{max.}$ 229 nm (ε 7850), τ 2.44 (1 H, dd, J 3 and 6 Hz, 3-H), 3.90 (1 H, d, J 6 Hz, 2-H), 6.80 (1 H, m, 9a-H), 7.44—7.60 (3 H, complex), 7.78 (2 H, m), 8.00 (1 H, d, J 11 Hz), 8.46—8.72 (7 H, complex), and 8.86 (2 H, s), *m/e* 214 (M^+, 31%), 186 (9), 147 (33), 133 (100), 91 (45), 82.5 (*m**, 214 ⟶ 133), and 67 (42).

endo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-1-exo-*ol* (20).—The allylic alcohol (16) (5.00 g) in ethanol (70 ml) was hydrogenated (1 atm; 3 h) at 20 °C over 5% rhodium–alumina (2.0 g). After filtration through Celite the solution was evaporated, and the residue in chloroform was chromatographed on a short column of silica gel to afford the *alcohol* as needles (4.28 g, 85%), m.p. 138—140° (with sublimation) (Found: C, 82.7; H, 10.1 $C_{15}H_{22}O$ requires C, 82.6; H, 10,1%), $\nu_{max.}$ 3630, 1158, 1070, 1030, and 950 cm^{-1}, τ 5.86 (1 H, m, $W_{\frac{1}{2}}$ 5 Hz, 1-H), 7.48 (1 H, m, 9a-H), 7.7—8.05 (5 H, complex), 8.1—8.7 (11 H, complex), and 8.7—8.9 (4 H, complex, 10- and 11-H), *m/e* 218 (M^+, 32%), 134 (100), 91 (76), 83 (70), 67 (89), and 66 (79)

endo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-1-*one* (21).—The alcohol (20) (2.00 g) in ether (120) was stirred with acidified 2N-sodium dichromate (10 ml) for 3 h at 20 °C. The usual work-up afforded the *ketone* as rods (1.68 g, 85%), m.p. 82.5—83.5° (from acetone) (Found: C, 83.5; H, 9.4. $C_{15}H_{20}O$ requires C, 83.3; H, 9.3%), $\nu_{max.}$ 1725 and 1177 cm^{-1}, τ 7.3—7.6 (2 H, complex, 9- and 9a-H), 7.65—8.45 (9 H, complex, 2-, 3-, 3a-, 4-, 4a-, 5-, and 8-H), 8.5—8.65 (4 H, complex, 6- and 7-H), and 8.7—8.9 (5 H, complex, 8a-, 10-, and 11-H), *m/e* 216 (M^+, 65%), 134 (70), 106 (80), 91(69), 83(100), and 66(56).

endo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-1-

endo-*ol* (22).—The ketone (21) (140 mg) in ethanol (10 ml) was stirred with sodium borohydride (40 mg) for 1 h at ambient temperature. The usual work-up afforded the *alcohol* as needles (125 mg, 90%), m.p. 137—138° (from hexane) (Found: C, 82.4; H, 10.1. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%), $\nu_{max.}$ 3640, 3450br, 1070, and 1043 cm^{-1}, τ 5.75 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, 1-H), 7.55—8.0 (8 H, complex, 3a-, 4-, 4a-, 5-, 8-, 8a-, 9-, and 9a-H), 8.05—8.7 (9 H, complex), and 8.7—9.0 (4 H, complex, 10- and 11-H), *m/e* 218 (M^+, 46%), 200 (29), 134 (74), 91 (73), 82.5 (*m**, 218 ⟶ 134), 67 (100), 66 (66), and 62 (*m**, 134 ⟶ 91).

Reaction of the Olefin (15) *with* 9-*Borabicyclo*[3.3.1]*nonane*.—The olefin (2.34 g) was added to a 0.5M-solution of 9-borabicyclo[3.3.1]nonane in tetrahydrofuran (25 ml), under nitrogen, and the mixture was set aside under nitrogen at ambient temperature for 24 h. Sodium hydroxide (1.2 g) in water (5 ml) and hydrogen peroxide (30%; 4 ml) were then added, and the mixture was stirred at 60 °C under reflux. After 1 h further similar quantities of sodium hydroxide and hydrogen peroxide were added and stirring was continued for a further 1 h. The mixture was then diluted with ether, washed with aqueous sodium carbonate, and evaporated. The oily residue (4.5 g) was taken up in dichloromethane and chromatographed on silica to separate cyclooctane-1,5-diol from the required alcohols. Fractional crystallization of the latter mixture from cyclohexane afforded small samples of the 1-*exo*-alcohol (20) and the 2-exo-*alcohol* (23) as needles, m.p. 144° (Found: C, 82.3; H, 10.0. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%), $\nu_{max.}$ 3630 and 1050 cm^{-1}, τ 5.73 (1 H, quint, J 7 Hz, 2-H), 7.5 (1 H, m), 7.82 (2 H, m), 8.05 (2 H, m), 8.1—8.3 (5 H, complex), 8.4—8.7 (6 H, complex), and 8.7—8.95 (4 H, complex, 10- and 11-H), *m/e* 218 (M^+, 22%), 134 (100), 133 (41), 91 (74), 67 (77), and 66 (89). The *acetate* crystallised from light petroleum in prisms, m.p. 98—99° (Found: C, 78.5; H, 9.3. $C_{17}H_{24}O_2$ requires C, 78.4; H, 9.3%), $\nu_{max.}$ 1735, 1360, 1240, and 1040 cm^{-1}, τ 4.96 (1 H, quint, J 7 Hz, 2-H), 7.50 (2 H, m), 7.80 (2 H, m), 7.9—8.15 (2 H, complex), 8.05 (3 H, s, Ac), 8.2 (4 H, m), 8.4—8.7 (6 H, complex), and 8.7—9.0 (4 H, complex, 10- and 11-H).

endo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-2-*one* (24).—(a) The mixture of alcohols (1.60 g) obtained from the preceding experiment was dissolved in ether (50 ml) and stirred with acidified 2N-chromic acid (7 ml) at 25 °C for 1 h. The usual work-up afforded a crystalline mixture of ketones (1.2 g) which was separated by plate chromatography with dichloromethane–hexane (1 : 1) as solvent. The 1-ketone (21) was identified as the material (0.74 g, 1.6%) in the band of lower R_F value. The material of higher R_F on crystallization from light petroleum gave the 2-*ketone* as plates (0.54 g, 34%), m.p. 134—135° (Found: C, 83.4; H, 9.2. $C_{15}H_{20}O$ requires C, 83.3; H, 9.3%), $\nu_{max.}$ 1740, 1410, and 1170 cm^{-1}, τ 7.35 (2 H, m, 3a- and 9a-H), 7.85 (6 H, m), 7.9—8.2 (2 H, complex), 8.25—8.45 (2 H, complex), 8.5—8.7 (4 H, complex, 6- and 7-H), and 8.7—8.9 (4 H, complex, 10- and 11-H), *m/e* 216 (M^+, 15%), 134 (49), 105 (59), 92 (39), 91 (88), 79 (82), and 66 (100).

(*b*) The olefin (15) (1.50 g) was stirred in ether (20 ml) with lithium borohydride (150 mg) at 20 °C under nitrogen while a 48% solution of boron trifluoride in ether (330 mg) was added during 10 min. Stirring was continued for 3 h, and then water (5 ml) was added, followed by a solution (15 ml) of sodium dichromate (3.7 g) and sulphuric acid (3 ml) during 30 min. The mixture was stirred for a further 3 h, then worked up in the usual way to afford a solid (1.2 g), plate chromatography of which gave the 1-ketone (410 mg, 25%), the 2-ketone (350 mg, 22%), and *endo,exo,endo*-perhydro-4,9:5,8-dimethanobenz[*f*]indene (310 mg), m.p 48° (lit.,[2] 49°), identical with a specimen prepared by hydrogenation of cyclopentadiene trimer.

endo,exo,endo-*Perhydro*-4,5:9,8-*dimethanobenz*[f]*inden*-2-endo-*ol* (25).—The 2-ketone (24) (40 mg) was stirred with sodium borohydride (15 mg) in ethanol (4 ml) for 3 h, and the mixture was then worked up in the usual way. The *alcohol* (35 mg) crystallised from hexane in plates, m.p. 139—140° (Found: C, 82.4; H, 10.3. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%), $\nu_{max.}$ 3 640, 1 300, 1 160, 1 120, 1 100, 1 080, 1 065, and 1 050 cm^{-1}, τ 5.90 (1 H, m, $W_{\frac{1}{2}}$ 25 Hz, 2-H), 7.82 and 8.05 (8 H, 2m, 3a-, 4-, 4a-, 5-, 8-, 8a-, 9-, and 9a-H), 8.15—8.7 (9 H, complex), and 8.7—9.0 (4 H, complex, 10- and 11-H), *m/e* 218 (M^+, 2.5%), 200 (11), 134 (16), 132 (40), 105 (34), 91 (91), 79 (72), 77 (67), 68 (100), and 67 (78).

The *acetate* crystallised from light petroleum in rods, m.p. 115—116° (Found: C, 78.2; H, 9.2. $C_{17}H_{24}O$ requires C, 78.4; H, 9.3%), $\nu_{max.}$ 1735, 1365, 1230, and 1040 cm^{-1}, τ 5.04 (1 H, tt, J 5 and 9 Hz), 7.80 and 8.10 (8 H, 2m, 3a-, 4-, 4a-, 5-, 8-, 8a-, 9-, and 9a-H), 8.05 (3 H, s, Ac), 8.1—8.45 (4 H, complex, 1- and 3-H), 8.45—8.7 (4 H, complex, 6- and 7-H), and 8.7—8.95 (4 H, complex, 10- and 11-H).

endo,exo,endo-*Perhydro*-4,9:5,8-*dimethanobenz*[f]*inden*-3a-*ol* (26).—A solution of t-butyl perbenzoate (1.70 g) in benzene (90 ml) was added with stirring during 20 min to a refluxing solution of the olefin (15) (3.50 g) and copper(II) octanoate (20 mg) in benzene (90 ml) under nitrogen. After being refluxed for a further 24 h, the mixture was cooled, diluted with ether, and washed successively with dilute sulphuric acid, sodium carbonate solution, and water. Evaporation of the ethereal solution afforded a yellow oil (4.38 g), which was dissolved in ether (50 ml), treated with lithium aluminium hydride, and boiled under reflux for 2 h. The usual work-up afforded an oil (4.1 g) which was subjected to dry-column chromatography on silica gel with dichloromethane as solvent. The fraction of high R_F was starting material; that of R_F *ca.* 0.3 comprised a mixture of solid alcohols (1.5 g).

The latter in ethanol (60 ml) was hydrogenated (1 atm; 3 h) at 20 °C over 5% rhodium–alumina (2.0 g). The usual work-up afforded a solid (1.44 g) which was shown by g.l.c. to contain the 3a-alcohol (57%) and the 1-*exo*-alcohol (41%) and its *endo*-isomer (2%). The solid was dissolved in ether (20 ml) and treated in the usual way with acidified 2N-sodium dichromate (10 ml). Work-up afforded an oil which, when chromatographed in silica gel, gave the 1-ketone (21) (0.45 g. 24%) and the *alcohol* (26) (0.68 g, 36%), as laths, m.p. 136° (from hexane) (Found: C, 82.2; H, 10.2 $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%), $\nu_{max.}$ 3620, 1300, 1180, and 1040 cm^{-1}, τ 7.7—8.1 (7 H, complex), 8.1—8.35 (5 H, complex), 8.35—8.7 (7 H, complex), and 8.7—9.0 (4 H, complex, 10- and 11-H), *m/e* 218 (M^+, 2%), 135 (58), 134 (100), 93 (26), 91 (26), 84 (82), and 67 (26).

This work was mainly carried out in the Dyson–Perrins Laboratory while A. L. J. B. was on study leave from the University of Adelaide. We thank Professor Sir Ewart Jones for his interest, advice, and encouragement. One of us (A. L. J. B.) gratefully acknowledges the receipt of grants from the British Council and the Royal Society. M. G. thanks the S.R.C. for a studentship. Technical assistance was generously given by Mr. P. Beckwith.

[6/1092 *Received*, 9*th June*, 1976]