The Dimerisation of Some 4-Hydroxyindenes

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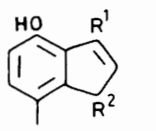
The acid-catalysed dimerisation of the indenes (**1**)—(**5**), has been studied and a number of products isolated. The structure and stereochemistry of these compounds has been established by the use of crossed dimers, ^{13}C-labelling, and ^1H and ^{13}C n.m.r. spectroscopy.

In 1979 we reported studies on the dimerisation of some hydroxyindenes,[1] the structure of one dimer being established unequivocally by *X*-ray crystallography. We have now submitted this reaction to more intensive scrutiny and, in collaborative studies, have established the structures of some of these dimers by the application of ^1H n.m.r. relaxation pathway analysis.[2] In this paper we report on the synthesis and interconversion of these dimers and their congeners, and on the application of ^{13}C n.m.r. spectroscopy to the structural elucidation of these compounds. All of these results are consistent with the proton relaxation studies.[2]

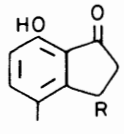
The desired indenes (**1**) and (**2**) were prepared in 80—90% yield by elimination of water from the corresponding tertiary alcohols, themselves derived by treatment of an indanone with methylmagnesium iodide. Work-up of the Grignard reaction required the addition of an ether-soluble base (*e.g.* triethylamine or di-isopropylamine) followed by aqueous work-up with buffer or dilute acid. As some starting material was always recovered, formation of the unreactive magnesium enolate must be occurring also. The lower homologue (**8**) was obtained in good yield from the indanone (**6**). Reaction of the indanone (**7**) gave two epimeric alcohols* (**9**) and (**10**) in the ratio of *ca.* 1:2. Crystallisation afforded fractions enriched in each isomer. Neither was obtained pure. The Grignard reagent is expected to attack *trans* to the 3-methyl group of (**7**) to give (**10**) as the major product and (**9**) as the minor product. Consistent with this expectation was the downfield chemical shift of the 1-methyl group in the ^1H n.m.r. spectrum (δ 1.65) of the *cis* dimethyl product (**9**), compared with a value of δ 1.52 in the *trans* isomer (**10**) and of δ 1.48 in the lower homologue (**8**). Similar results have been obtained with cyclohexanes.[3] The addition of butyl-lithium to indanones (**6**) or (**7**) gave good yields of alcohols. These gave i.r. and ^1H n.m.r. spectra consistent with their structures but the compounds did not crystallise and for convenience were converted into indenes prior to purification.

Although dehydration of the indanols is a facile process, the synthesis of the pure indenes uncontaminated by isomers or dimers required careful use of homogeneous conditions, *e.g.* dilute methanolic sulphuric acid. Similar treatment of the 1-butylindanols gave acceptable yields of butylindenes (**3**) and (**4**) but the product mixture from (**3**) contained up to 20% of the alkene (**11**), characterised as the exocyclic isomer by a $^4J_{HH}$ coupling of 7 Hz between the C-2 methylene protons and the C-1′ vinyl proton, much greater than that observed (1—2 Hz) in the endocyclic indenes. The (*E*)-stereochemistry is assumed for (**11**) as this stereoisomer should be the more stable. All of the endocyclic indenes (**1**)—(**4**) gave elemental analyses and spectra consistent with their structures, including the appropriate allylic and homoallylic coupling in their ^1H n.m.r. spectra.

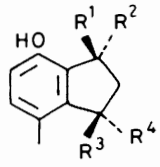
A systematic examination of the acid-catalysed reactions of the indenes was undertaken. Treatment of the 4-hydroxyindene (**1**) with 5% (v/v) trifluoroacetic acid in chloroform for 30 min



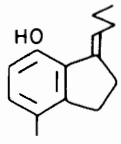
(**1**) R^1 = Me, R^2 = R^3 = H
(**2**) R^1 = R^2 = Me, R^3 = H
(**3**) R^1 = Bu, R^2 = R^3 = H
(**4**) R^1 = Bu, R^2 = Me, R^3 = H
(**5**) R^1 = R^3 = Me, R^2 = H



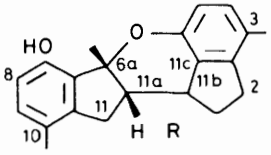
(**6**) R = H
(**7**) R = Me



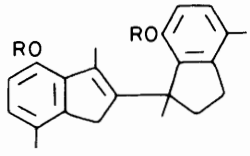
(**8**) R^1 = Me, R^2 = OH, R^3 = R^4 = H
(**9**) R^1 = R^3 = Me, R^2 = OH, R^4 = H
(**10**) R^1 = OH, R^2 = R^3 = Me, R^4 = H



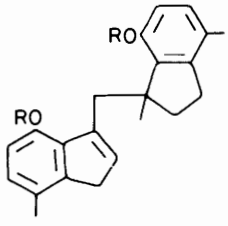
(**11**)



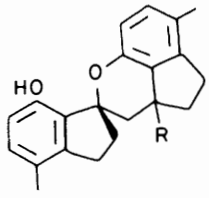
(**12**) R = α—Me
(**13**) R = β—Me



(**14**) R = H
(**15**) R = Me



(**16**) R = H
(**17**) R = Me



(**18**) R = β—Me
(**19**) R = α—Me

produced one crystalline dimer in 60% yield. It gave the molecular ion in the mass spectrum at *m/z* 320, analysed for $C_{20}H_{24}O_2$, and had ^1H and ^{13}C n.m.r. spectra suggestive of a pentacyclic dimer. Comparison of the ^1H n.m.r. chemical shifts of the signals due to the aliphatic methyl groups with those of the bromo compound (**28**) of known structure suggested the structure and stereochemistry (**12**); this was confirmed by the

* All compounds are racemic. Only one enantiomer is drawn.

Table 1. ^{13}C N.m.r. chemical shifts for di-indeno[7,1-*bc*:2′,1′-*e*]pyrans

6aβ, 11aβ, 11bβ-configuration

	(13)	(23)	(24)	(29)	(31)
3-Me	17.6	17.8	18.4	17.7	17.7
10-Me	18.1	18.5	18.7	18.1	18.0
6a-Me	29.1	30.5	30.5	28.6	28.9
11b-Me	26.8	30.5	28.2		
2-Me		22.1	20.4		21.9
11-Me		21.6	21.6		
C-1	37.4	44.5	46.4	38.5	41.8
C-2	29.4	38.8	38.2	30.2	39.1
C-6a	92.8	92.8	92.5	92.8	92.9
C-11	34.0	41.3	41.2	34.0	34.5
C-11a	56.1	67.1	66.7	53.1	51.2
C-11b	43.8	43.8	42.5	47.8	48.0
C-10	130.6	131.9	131.9	130.6	130.6
C-3	134.8	135.2	135.8	134.7	135.3
C-9	130.6	131.9	131.9	130.6	130.6
C-4	129.7	129.4	129.9	128.5	129.4
C-8	114.2	114.4	114.5	114.1	114.7
C-5	113.9	114.4	113.9	113.6	114.1
C-7	151.1	151.2	151.2	151.0	151.1
C-5a	149.8	149.7	149.5	149.9	150.3
C-6b	124.9	124.9	125.0	124.9	125.0
C-11c	126.9	127.3	127.6	127.0	127.0
C-10a	141.3	145.4	145.1	141.1	141.3
C-2a	141.0	144.9	144.0	141.9	146.0

6aβ, 11aβ, 11bα-configuration

3-Me	18.2	17.7	18.7	18.1	18.1
10-Me	17.7	17.5	17.5	17.8	17.6
6a-Me	27.7	30.1	30.4		
11b-Me	18.7	21.8	18.9	18.6	18.8
2-Me		21.8	19.9		
11-Me		21.0	20.9		20.5
C-1	41.8	49.2	51.8	41.6	41.6
C-2	29.3	38.6	38.3	29.2	29.3
C-6a	92.8	92.9	92.6	95.3	95.3
C-11	31.5	39.5	39.6	31.8	39.6
C-11a	58.8	68.3	67.8	56.4	64.4
C-11b	43.3	43.7	42.1	43.1	43.6
C-10	130.6	130.2	130.2	130.0	129.9
C-3	136.1	137.4	137.5	135.7	136.3
C-9	130.4	131.2	131.2	130.3	131.1
C-4	128.9	129.5	130.0	128.9	128.9
C-8	114.0	114.8	114.8	113.6	113.6
C-5	114.4	115.1	114.3	114.4	114.8
C-7	150.7	150.9	150.8	151.0	151.2
C-5a	148.9	149.0	148.7	149.5	149.7
C-6b	124.9	124.7	124.8	124.7	124.8
C-11c	127.1	127.5	127.8	126.8	126.9
C-10a	139.4	144.6	144.7	139.8	144.4
C-2a	141.0	144.9	143.7	140.9	140.6

^1H n.m.r. relaxation studies[2] and by ^{13}C n.m.r. spectral comparisons (Table 1). A second dimer was also isolated, albeit in low yield. However, it was found that the yield could be increased greatly by appropriate choice of conditions since this dimer was less stable but was formed more rapidly than dimer (**12**). Thus, reaction of the indene (**1**) with 0.2% trifluoroacetic acid in chloroform for 90 min gave the new dimer in 60% yield. The analytical and spectral properties suggested structure (**13**). Specifically, in the dimer (**12**) the 11b-methyl group is situated under the phenolic ring, and consequently resonates at higher field (δ_H 0.71) than the corresponding methyl group in (**13**) (δ_H 1.40) (Figure 1). In the ^{13}C n.m.r. spectrum of the 11b-epimer (**13**) the *gauche* arrangement of the methyl group at C-11b and the vicinal proton at C-11a causes this methyl group to resonate at δ_C 26.8, 8.6 p.p.m. downfield from that in (**12**) (*cf.* ref. 4).

The dimerisation of (**1**) is well suited to ^1H n.m.r. analysis as

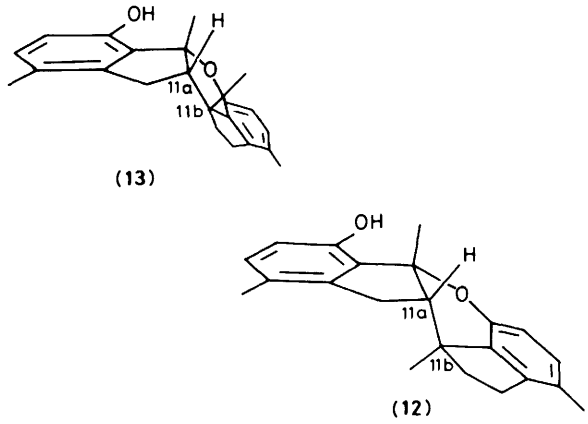


Figure 1.

the rate is dependent on acid concentration, which can be adjusted readily. Addition of 0.02 ml of 5% trifluoroacetic acid in tetrachloromethane to a solution of the hydroxyindene (**1**) (60 mg) in deuteriochloroform (0.48 ml) resulted in a rapid (5 min) decrease in monomer concentration and production of dimer (**13**). A small amount of dimer (**12**) was present also and this increased with time at the expense of (**13**), so that after 70 h the former predominated in the ratio 2:1. During this relatively slow isomerisation, an intermediate product was formed, as evidenced by a singlet peak at δ_H 1.52, subsequently assigned to the methyl group on an sp^3 carbon in the tetracyclic compound (**14**). This dimer had an initial rate of formation just less than that of (**12**), and its concentration never exceeded that of dimer (**13**). As the concentration of the thermodynamically favoured product (**12**) increased, the concentration of both (**13**) and (**14**) decreased together and after 120 h the ratio of the three dimers, (**12**), (**13**), and (**14**) was *ca.* 10:1:1, by which time the 4-hydroxyindene (**1**) could not be detected.

The dimerisation also occurred in the presence of Lewis acids. For example, iodine in tetrachloromethane gave similar results, although the amount of the uncyclised dimer (**14**) was reduced. In contrast, under more polar conditions using a protic acid the equilibrium position favours the uncyclised dimer (**14**). Treatment of hydroxyindene (**1**) with sulphuric acid in aqueous methanol for 3 h under reflux gave a mixture which consisted mainly of the uncyclised dimer (**14**) (65%) and starting material (**1**) (20%). Dimer (**12**) was present in small amounts (<5%) while the stereoisomer (**13**) could not be detected. A small amount of another uncyclised dimer, probably (**16**), was present also. A reaction mixture of almost identical composition was obtained by treatment of dimer (**12**) with trifluoroacetic acid in aqueous methanol, indicating that the mixtures obtained reflect the equilibrium composition. Preparative t.l.c. of this latter reaction mixture yielded uncyclised dimer (**14**) of reasonable purity, although it could not be crystallised. The compound showed the expected spectral properties, including signals at δ_C 136.2 and 141.9 assigned to the two quaternary alkene carbons, while in the ^1H n.m.r. spectrum the vinylic methyl group resonated as a triplet (*J* 2 Hz) at δ_H 2.04. When the tetracyclic compound (**14**) was treated with trifluoroacetic acid in deuteriochloroform, dimers (**12**) and (**13**) were formed, initially at similar rates, but as the ratio of (**12**), (**13**), and (**14**) approached 1:1:1, dimer (**12**) began to predominate and the usual equilibrium mixture for these conditions was eventually obtained.

For comparison, the dimerisation that occurs concomitantly when samples of the alcohol (**7**) undergo elimination of water was investigated. Evaporation of methanol from a solution of (**8**) gave a viscous oil which on occasional warming gave a

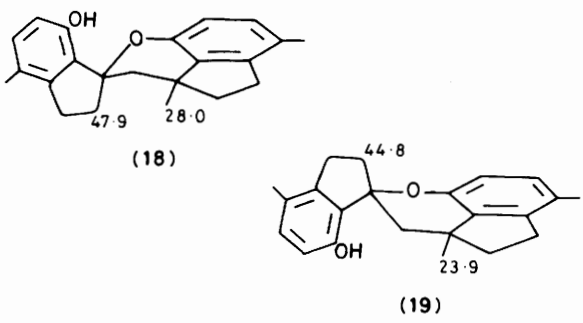


Figure 2.

product mixture typically containing the 4-hydroxyindene (**1**) (*ca.* 20%), together with dimers (**12**) (< 5%), (**13**) (< 10%), (**14**) (< 10%), and (**16**) (< 10%). However, in addition, two new dimers, assigned structures (**18**) and (**19**), were each present in up to 20% yield. These new dimers arise *via* the product of kinetically favoured elimination, the exocyclic alkene (**20**); in the absence of solvent this product is at its maximum concentration, and direct dimerisation then competes effectively with isomerisation to the endocyclic indenol (**1**). The spiro dimers (**18**) and (**19**), showed the expected spectral properties; in particular, they displayed signals due to only three methyl groups and five methylene groups. The assignments of relative configuration are based on a comparison of the ^{13}C n.m.r. chemical shifts, which rely on reasonable inferences of the preferred conformations. The differing environments of the C-2′ and C-3a methyl groups are reflected in their ^{13}C n.m.r. chemical shifts, with the δ-synaxial relationship of these two groups in (**18**) causing the observed deshielding (Figure 2).

Although dimers (**18**) and (**19**) were never isolated from acid-catalysed solution reactions, nevertheless their solution chemistry under these conditions was examined. When either spiro isomer was treated with dilute trifluoroacetic acid in deuteriochloroform rapid equilibration occurred to give a mixture (1:3) of (**18**) and (**19**). This mixture of spiro dimers then underwent slow ring opening to give the tetracycle (**16**). Alternatively, treatment of the mixture of spiro dimers with more concentrated acid led to (**12**), (**13**), and (**14**), and finally to the equilibrium mixture of these dimers. Clearly, if (**18**) and (**19**) are formed during reactions in solution, they do not accumulate but isomerise to other dimers. The uncyclised dimer (**14**) could be isolated in high yield following brief exposure of a mixture of (**18**) and (**19**) to trifluoroacetic acid in methanol–dichloromethane. A minor product from this reaction was identified (^1H n.m.r.) as the exocyclic alkene dimer (**21**).

Dimerisation of the 4-methoxyindene (**5**), which cannot lead to pentacyclic products, produced two tetracyclic compounds. Thus, treatment of the methoxyindanol (**22**) with 5% trifluoroacetic acid in methanol effected rapid elimination to give (**5**) which reacted further to give the dimers (**15**) and (**17**), the latter compound being formed *via* the exocyclic alkene.

With the structure and stereochemistry of the dimers of the 4-hydroxyindene (**1**) established, we investigated the more complex case of the methyl homologue (**2**). Only two of the four possible racemic diastereomeric pentacyclic dimers, *viz* (**12**) and (**13**), were isolated from the acid-catalysed reaction of (**1**) in solution, so the introduction of the additional two chiral centres in the dimers of the 1-methylindene (**2**) led to the expectation of eight racemic stereoisomers. In fact, only four were isolated, and these were assigned structures (**23**), (**24**), (**25**), and (**26**), the latter two being identical with those reported previously.[1] The four dimers were paired according to chromatographic mobility, chemical stability, and n.m.r. spectral characteristics. The two known dimers (**25**) and (**26**), which could not be separated chromatographically, closely resembled the lower homologue (**12**), whereas the new compounds have lower R_F values and resemble dimer (**13**). On the hypothesis that the similarity in chemical properties mirrors a similarity in ring junction stereochemistry, it was assumed that the structural variations must lie in the stereochemistry of the methyl groups at either C-2 or C-11, or both. The configuration at these centres was established using ^{13}C n.m.r. chemical shift data (see Table 1), the assignments of signals having been established by the use of crossed dimers derived from the 3-butyl-4-hydroxyindenes (**3**) and (**4**) with their lower homologues (**1**) and (**2**), and by the dimerisation of 4-hydroxyindenes in which the C-3 methyl group was enriched with ^{13}C. Further evidence was adduced from the values of certain $^3J_{HH}$ coupling constants (see Table 3). All of this evidence was self-consistent and was confirmed by the ^1H n.m.r. relaxation studies. The structure of the bromo derivative of one dimer, determined previously by *X*-ray diffraction studies, was confirmatory and led to a correction of the spectral assignments reported earlier.[1]

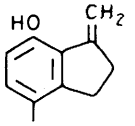
Co-dimerisation of either of the 3-methyl-4-hydroxyindenes (**1**) and (**2**) with either of the 3-butyl-4-hydroxyindenes (**3**) and (**4**), under conditions to maximise the formation of crossed dimers with the desired ring-junction stereochemistry, gave a series of compounds whose regiochemistry [*e.g.* (**30**) *vs.* (**36**)] could be determined by mass spectroscopy of the 8-bromo derivatives [*e.g.* (**38**)]. Bromination of any of these products in aqueous dioxane results in the introduction of one bromine atom into the phenolic ring. Electron-impact induced fragmentation reverses the dimerisation and produces, in high relative intensity, bicyclic bromine-containing ions bearing the introduced alkyl substituent (Me or Bu).

Parallels between the ^1H n.m.r. chemical shifts of the methyl groups in the dimers (**12**) and (**13**) and in the various crossed dimers indicated close stereochemical similarities. Thus the methyl group at C-6a in (**29**) resonates further downfield (δ_H 1.92) than that in the epimeric crossed dimer (**30**) (δ_H 1.46), correlating with the difference observed between the dimers (**13**) (6a-Me, δ_H 2.00) and (**12**) (6a-Me, δ_H 1.56).

The crossed dimerisation of the 3-butyl-1-methylindene (**4**) with the 3-methylindene (**1**) produced only compound (**33**), whereas reaction of the 3-butylindene (**3**) with the 1,3-dimethylindene (**2**) produced, besides the tetramethyl dimers (**25**) and (**26**), an inseparable mixture of crossed dimers (**34**) and (**35**). Taken together, these two experiments suggest that the inseparable pairs of dimers differ only in their stereochemistry at C-2.

The absence of a methyl group at C-6a in the crossed dimer (**36**) allows the signals occurring at *ca.* δ_C 30 in the ^{13}C n.m.r. spectra of the other dimers to be assigned unequivocally to this group, since the methyl groups at C-2, C-3, C-10, C-11, and C-11b all resonate at higher field than δ_C 22.

^{13}C-Labelled compounds allowed the signal due to the methyl group at C-11b to be distinguished from other upfield peaks in dimers (**25**) and (**26**). A mixture (1:1) of these dimers, prepared by the addition of ^{13}C-labelled methylmagnesium iodide to the indanone (**7**), followed by the usual elimination and dimerisation sequence, was labelled equally on the 6a-methyl and 11b-methyl groups. The ^{13}C n.m.r. spectrum of the inseparable mixture of (**25**) and (**26**) showed greatly enhanced signals at δ_C 18.8 (**26**) and 21.8 (**25**) (11b-Me), and 30.2 (**25**) and 30.4 (**26**) (6a-Me). The structural assignments to dimers (**25**) and (**26**) had been made possible by the crystallisation and examination of the two individual compounds in separate experiments, while the stereochemical assignments were based on the chemical shift data reported in Table 2. Of particular significance was the downfield shift produced by a δ-synaxial group; such an interaction of methyl groups in cyclohexanes



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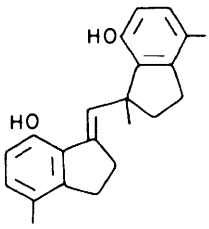

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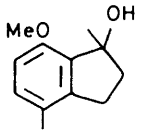

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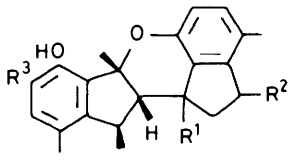
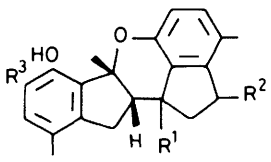
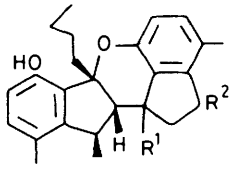


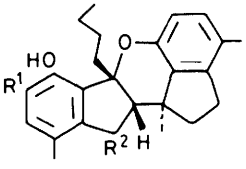
(23) $R^1 = R^2 = \beta$-Me, R^3 = H
(24) $R^1 = \beta$-Me, $R^2 = \alpha$-Me, R^3 = H
(25) $R^1 = R^2 = \alpha$-Me, R^3 = H
(26) $R^1 = \alpha$-Me, $R^2 = \beta$-Me, R^3 = H
(27) $R^1 = \alpha$-Me, $R^2 = \beta$-Me, R^3 = Br
(28) $R^1 = R^2 = \alpha$-Me, R^3 = Br



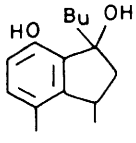
(29) $R^1 = \beta$-Bu, R^2 = H, R^3 = H
(30) $R^1 = \alpha$-Bu, R^2 = H, R^3 = H
(31) $R^1 = \beta$-Bu, $R^2 = \beta$-Me, R^3 = H
(32) $R^1 = \beta$-Bu, R^2 = H, R^3 = Br



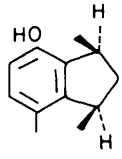
(33) $R^1 = \alpha$-Me, R^2 = H
(34) $R^1 = R^2 = \alpha$-Me
(35) $R^1 = \alpha$-Me, $R^2 = \beta$-Me
(36) $R^1 = \alpha$-Me, R^2 = H



(37) $R^1 = R^2$ = H
(38) R^1 = Br, $R^2 = \beta$-Me
(39) R^1 = H, $R^2 = \beta$-Me



(40)



(41)

produces deshielding effects of 3.2—4.6 p.p.m.[5] Smaller effects are seen in the 4-hydroxyindene dimers since the methyl groups on the five-membered rings are pseudoaxial and hence further apart.

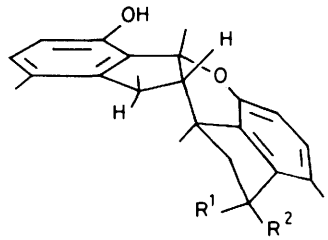
Confirmation of the assignment of the signals due to the methyl groups in the ^{13}C n.m.r. spectrum was provided by heteronuclear decoupling, since the methyl group at C-11b in (**24**) could be assigned unequivocally in the ^1H n.m.r. spectrum by comparison with the spectra of the crossed dimers (**29**) and (**31**), in which this group is absent.

The δ-effect in the molecules with 6aβ, 11aβ, 11bβ stereochemistry is slightly smaller than that in the other series,

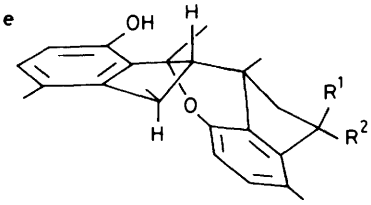
Table 2.

	(11)	(25)	(26)		(37)	(39)
δ_C 6a-Me	27.7	30.1	30.4	C-1′	41.6	44.9
δ Effect		+2.4	+2.7			+3.3
δ_C 11b-Me	18.7	21.8	18.9		18.6	18.8
δ Effect		+3.1				

	(12)	(23)	(24)		(29)	(31)
δ_C	29.1	30.5	30.5		28.6	28.6
δ Effect		+1.4	+1.4			
δ_C 11b-Me	26.8	30.5	28.2	C-1′	38.5	41.8
δ Effect		+3.7	+1.4			+3.3



(23) R^1 = Me, R^2 = H
(24) R^1 = H, R^2 = Me



(25) R^1 = Me, R^2 = H
(26) R^1 = H, R^2 = Me

Figure 3.

where the 11b substituent is in the α-orientation, since the relevant methyl groups are further apart.

Although it is not possible to assign the conformations definitely, the values of the $^3J_{HH}$ coupling constants (Table 3) are consistent with likely conformations. In the 6aβ, 11aβ, 11bβ dimers the 11aβ-H, 11α-H angle is *ca.* 90° and no coupling is observed. In the 6aβ, 11aβ, 11bβ dimers this angle is larger as both the 11aβ, 11β-H and 11aβ, 11α-H coupling constants have increased. These relationships are consistent with those predicted by the Karplus equation, although the system is not ideal because of the ring strain on the carbon–carbon bond through which coupling occurs.

Another feature consistent with the conformational analysis is the $^3J_{HH}$ coupling constants of the methyl groups at C-11 and C-2 with their respective geminal protons. In the cyclohexanes[6] it is known that the coupling constant of an axial methyl group with a geminal equatorial proton (7.0—7.3 Hz) is greater than that of an equatorial methyl group with a geminal axial proton (6.3—7.0 Hz). A similar effect occurs in these dimers. Thus in dimer (**25**) both the 11β- and 2α-methyl groups are pseudoaxial and show a coupling constant with the respective geminal proton of 7.22 Hz, while in the diastereoisomer (**26**) the pseudoaxial 11β-methyl groups shows 7.22 Hz coupling and the pseudoequatorial 2β-methyl group has 6.88 Hz coupling. In dimer (**24**) both the 2α- and the 11β-methyl groups are pseudoequatorial and show couplings of 6.76 and 6.99 Hz, respectively. The pseudoequatorial 11β-methyl group in dimer

Table 3. ^{1}H N.m.r. spectra of indene dimers (400 MHz). The table gives chemical shifts (p.p.m.), multiplicity, and observed coupling constants (Hz)

Assignment	(13)	(12)	(23)	(24)	(25)	(26)
2-Me			1.39 d, 7.22	1.33 d, 6.76	1.36 d, 7.22	1.40 d, 6.99
3-Me	2.03	2.21	2.08	2.11	2.26	2.31
6a-Me	1.99	1.57	2.01	2.01	1.63	1.70
10-Me	2.13	2.22	2.17	2.22	2.27	2.26
11-Me			1.35 d, 6.99	1.36 d, 6.99	1.35 d, 7.22	1.37 d, 7.22
11b-Me	1.40	0.71	1.53	1.35	0.92	0.73
11a-H	2.95 (obs.)	2.38 d, 6.76	2.42 d, 5.13	2.43 d, 4.66	1.91 s	2.03 s
11α-H	2.52 d × d 16.05, 5.65	2.87—2.98 m	2.82—2.88 m	3.05—3.08 m	3.33—3.39 m	3.36 q, 7.22
11β-H	2.78 d × d 16.05, 8.82	2.87—2.98 m				
1-H_2	2.87—3.01 m	1.84—1.92 m 2.12—2.17 m	1.67 d × d 13.7, 1.63 2.68 d × d 13.7, 9.7	1.86 d × d 8.6, 13.1 2.19—2.24 m	1.86 d × d 13.9, 1.1 2.26—2.32 m	1.51—1.57 m 2.38 d × d 6.99, 12.3
2-H	2.15—2.22 m 1.94—2.02 m	2.77—2.83 m 2.99—3.05 m	3.28—3.36 m	3.48—3.56 m	3.33—3.39 m	3.45—3.51 m
4-H	6.83 d, 8.14	6.92 d, 7.92	6.80 d, 8.15	6.82 d, 8.15	6.98 d, 8.25	6.97 d, 8.15
5-H	6.51 d, 7.9	6.69 d, 7.92	6.47 d, 8.38	6.58 d, 8.15	6.72 d, 8.15	6.68 d
8-H	6.57 d, 7.91	6.69 d, 8.15	6.58 d, 7.92	6.48 d, 7.92	6.71 d, 7.69	6.71 d
9-H	6.75 d, 7.91	6.92 d, 8.15	6.72 d, 7.92	6.72 d, 7.92	6.92 d, 7.92	6.89 d, 7.92

(**23**) shows coupling of 6.99 Hz, while the pseudoaxial 2β-methyl group shows 7.22 Hz coupling (Figure 3).

The formation and interconversion of the dimethyl indenol dimers (**23**), (**24**), (**25**), and (**26**) was followed conveniently by ^{1}H n.m.r. spectroscopy. When a solution of the dimethyl indenol (**2**) was treated in tetrachloromethane for 5 min with 1% (v/v)trifluoroacetic acid, rapid conversion occurred to give dimer (**23**) almost exclusively (^{1}H n.m.r.) (60% isolated yield). After a reaction time of 3 h, slow isomerization of (**23**) led to a mixture of dimers (**23**), (**24**), (**25**), and (**26**) in a ratio of approximately 1:1:1:0.1, while after 90 h this ratio became almost stationary at 1:1:20:2; after a further 1 000 h the proportion of dimer (**26**) almost doubled. When the concentration was increased to 5% trifluoroacetic acid in tetrachloromethane and the mixture was heated under reflux for 2 h, the ratio of the four dimers became 1:1:10:10. Because similar treatment of a mixture enriched in dimer (**26**), the slowest forming compound, gave an identical distribution of products, this ratio is the equilibrium composition under these conditions. As a consequence of these kinetic and thermodynamic properties, it is possible to obtain dimer (**23**) almost free of dimer (**24**), from which it is inseparable by chromatography, by quenching the dimerisation after 5 min. Similarly, after 3 h, dimer (**25**) is obtained predominantly and can be purified readily by recrystallisation.

Experimental

M.p.s were determined with a Reichert-Kofler hot-stage apparatus. I.r. spectra were recorded with Perkin-Elmer 337 or 397 spectrometers, ^{1}H n.m.r. spectra with a Varian T60 spectrometer (60 MHz) or a Bruker WH-400 spectrometer (400 MHz), and ^{13}C n.m.r. spectra with a JEOL JNM-FX60 Fourier-transform spectrometer. Low resolution mass spectra were measured on a Varian-MAT CH7 mass spectrometer and high resolution spectra were measured on an AEI MS30 mass spectrometer. All compounds are racemic. Relative configuration is specified by α, β designations but, where this is inapplicable, as with spiro compounds, *R**, *S** designations are employed. Ether refers to diethyl ether.

The preparations and analytical figures for compounds (**12**), (**13**), (**23**), (**24**), (**25**), and (**26**) are reported in ref. 2.

2,3-*Dihydro*-1,4-*dimethyl*-1H-*indene*-1,7-*diol* (**8**).—The ketone (**6**)[7] (1 g, 6.2 mmol) in ether (30 ml) was added to methylmagnesium iodide (14 mmol) in ether (50 ml) at 0 °C under nitrogen. The mixture was stirred for 4 h at room temperature and triethylamine (2 ml, 20 mmol) was added followed by phosphate buffer (2 mol l^{-1}, pH 7; 200 ml). Ether extraction and work-up gave the crude product (1.05 g) which contained the alcohol (**8**) and starting material (**6**) (10—15%) (^{1}H n.m.r. and t.l.c.). Purification by p.l.c. gave the *alcohol* (**8**), m.p. 109—110 °C (from hexane–ether) (Found: C, 74.3; H, 8.2. $C_{11}H_{14}O_2$ requires C, 74.1; H, 7.9%); $\nu_{max.}$ 3 460 cm^{-1} (OH); δ_H 1.48 (3 H, s, 1-Me), 2.10 (3 H, s, 4-Me), 2.0—2.4 (2 H, m, 2-H_2), 2.5—2.9 (2 H, m, 3-H_2), 6.46 (1 H, d, *J* 8 Hz, 5-H), 6.80 (1 H, d, *J* 8 Hz, 6-H), and 5.3 (2 H, br s, 1-OH, 7-OH); δ_C 17.5 (4-Me), 26.2 (1-Me), 28.3 (C-3), 42.4 (C-2), 83.0 (C-1), 113.8 (C-6), 125.5 (C-7a), 130.0 (C-5), 131.9 (C-4), 141.1 (C-3a), and 150.7 (C-7); *m/z* 178 (M^+, 20%), 160 (100), and 145 (10).

3,7-*Dimethyl*-1H-*inden*-4-*ol* (**1**).[1]—Aqueous sulphuric acid (0.1 mol l^{-1}; 1 ml) in methanol (20 ml) was added to the alcohol (**8**) (0.45 g) in methanol (25 ml) at room temperature. After 30 min, excess of aqueous sodium hydrogen carbonate was added and most of the solvent was removed under reduced pressure. Work-up gave the crude product (0.4 g) which was purified by p.l.c. to give indene (**1**) (0.225 g, 56%), m.p. 102.5—103.5 °C (from pentane) (lit.,[1] 101.5—102 °C); δ_C ($CDCl_3$ + 2% Et_3N) 16.4 (3-Me), 17.7 (7-Me), 36.9 (C-1), 114.1 (C-5), 125.3 (C-3a), 126.6 (C-6), 127.2 (C-2), 131.6 (C-7), 139.9 (C-3), 145.7 (C-7a), and 148.8 (C-4).

2,3-*Dihydro*-1,3′,4,7′-*tetramethyl*-1,2′-*bi*-1H-*indene*-4′,7-*diol* (**14**).—Sulphuric acid (2 mol l^{-1}; 10 ml) was added to the alcohol (**8**) (0.55 g) in methanol (40 ml) at room temperature. After 90 min, water (200 ml) was added and work-up gave the crude product (0.48 g). Purification by p.l.c. gave the bi-indene (**14**) (0.25 g, 50%) as an amorphous solid; δ_H ($CDCl_3$) 1.52 (3 H, s, 1-Me), 2.04 (3 H, t, *J* 2 Hz, 3′-Me), 2.20 and 2.25 (2 × 3 H, 2 s, 4-Me, 7′-Me), 2.2 (2 H, m, 2-H_2), 2.9 (2 H, m, 3-H_2), 3.4 (2 H, m, 1′-H_2) 6.32—6.90 (4 H, 4 d, *J* 9 Hz, ArH), and 5.0 (2 H, br s, 4′-OH, 7-OH); δ_C 14.1 (3′-Me), 17.7, 18.2 (4-Me, 7′-Me), 25.3 (1-Me), 29.5 (C-3), 39.6 (C-2), 42.3 (C-1′), 48.3 (C-1), 114.0, 114.5 (C-5′, C-6), 124.9 (C-7a), 126.2 (C-3a′), 126.4 (C-6′), 129.0 (C-5), 132.4 (C-7′), 135.7 (C-4), 136.2 (C-3′), 141.9 (C-2′), 142.4 (C-7a′), 143.4 (C-3a), 148.6 (C-4′), and 149.9 (C-7); *m*/*z* 320 (M^+, 12%), 318 (14), 3 093 (24), and 161 (100).

2,3-*Dihydro*-7-*methoxy*-4-*methyl*-1H-*inden*-1-*one*.—Dimethyl sulphate (1.7 ml, 18 mmol) was added to the hydroxyindanone (**6**) (3.0 g, 17 mmol) in acetone (50 ml) over anhydrous potassium carbonate (2.58 g, 20 mmol) under an atmosphere of nitrogen. The mixture was heated under reflux for 18 h, and then cooled and filtered. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane, washed with dilute sulphuric acid, water, and brine, and dried ($MgSO_4$). Removal of solvent gave the *methoxyindanone* (2.35 g, 72%), m.p. 107—108 °C (from hexane–dichloromethane) (Found: C, 74.8; H, 7.05. $C_{11}H_{12}O_2$ requires C, 74.95; H, 6.9%); $\nu_{max.}$ (CCl_4) 1 720 cm^{-1} (CO); δ_H ($CDCl_3$) 2.25 (3 H, s, 4-Me), 2.76 (4 H, m, 2-H_2, 3-H_2), 3.88 (3 H, s, 7-OMe), 6.66 (1 H, d, *J* 8 Hz, 6-H), and 7.26 (1 H, d, *J* 8 Hz, 5-H).

2,3-*Dihydro*-7-*methoxy*-1,4-*dimethyl*-1H-*inden*-1-*ol* (**22**).—The above methoxyindanone (0.5 g, 2.8 mmol) in ether (20 ml) and tetrahydrofuran (5 ml) was added to methylmagnesium iodide (11 mol) in ether (4 ml). The mixture was stirred and heated under reflux for 1 h and then cooled and added slowly to a stirred mixture of ice and sodium acetate (1 mol l^{-1})–acetic acid (1 mol l^{-1}) buffer. Work-up gave the *methoxy alcohol* (**22**) (0.51 g, 93%), m.p. 58—59 °C (from hexane) (Found: C, 74.7; H, 8.6. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%); δ_H ($CDCl_3$) 1.60 (3 H, s, 1-Me), 2.16 (3 H, s, 4-Me), 2.1—3.0 (4 H, m, 2-H_2, 3-H_2), 3.2 (1 H, br s, exch. on deuteriation, 1-OH), 3.80 (3 H, s, 7-OMe), 6.58 (1 H, d, *J* 8 Hz, 5-H), and 6.94 (1 H, d, *J* 8 Hz, 6-H); *m*/*z* 192 (M^+ 7%), 177 (29), 174 (100), and 159 (24).

4-*Methoxy*-3,7-*dimethyl*-1H-*indene* (**5**).—Aqueous sulphuric acid (2 mol l^{-1}; 2 ml) was added to the alcohol (**22**) (0.22 g) in methanol (12 ml). The solution was left at room temperature for 30 min and then diluted with water. Ether extraction, work-up, and p.l.c. gave the indene (**5**) (0.116 g, 59%), b.p. 85 °C at 0.5 mmHg, m.p. 26—27 °C (Found: M^+ 174.1055. $C_{12}H_{14}O$ requires *M*, 174.1045); δ_H (CCl_4) 2.22 (3 H, s, 7-Me), 2.28 (3 H, m, $W_{\frac{1}{2}}$ 7 Hz, 3-Me), 3.02 (2 H, m, $W_{\frac{1}{2}}$ 7 Hz, 1-H_2), 3.76 (3 H, s, 4-OMe), 5.86 (1 H, m, $W_{\frac{1}{2}}$ 6 Hz, 2-H), 6.48 (1 H, d, *J* 8 Hz, 5-H), and 6.76 (1 H, d, *J* 8 Hz, 6-H); δ_C 16.6 (3-Me), 17.7 (7-Me), 36.9 (C-1), 55.5 (4-OMe), 109.3 (C-5), 125.5 (C-3a), 126.5 (C-6), 127.1 (C-2), 133.1 (C-7), 140.8 (C-3), 145.6 (C-7a), and 153.2 (C-4). The conversion of (**22**) into (**5**) could also be achieved by adsorption of the alcohol on silica gel and elution with hexane.

2,3-*Dihydro*-4′,7-*dimethoxy*-1,3′,4,7′-*tetramethyl*-1,2′-*bi*-1H-*indene* (**15**).—Trifluoroacetic acid (0.5 ml) was added to the alcohol (**22**) (1.0 g) in methanol (9 ml) and the solution was left for 1 h at 40 °C and for 2 h at room temperature. The crystalline precipitate was filtered off and washed with methanol to give the *dimer* (**15**) (0.27 g), m.p. 137—138 °C (from ether–methanol) (Found: C, 82.9; H, 8.2. $C_{24}H_{28}O_2$ requires C, 82.7; H, 8.1%); δ_H ($CDCl_3$) 1.62 (3 H, s, 1-Me), 1.96 (3 H, t, *J* 2 Hz, 3′-Me), 2.24 (6 H, s, 4-Me, 1-Me, 7′-Me), 2.0—3.0 (4 H, m, 2-H_2, 3-H_2), 3.2 (2 H, m, $W_{\frac{1}{2}}$ 7 Hz, 1′-H_2), 3.60 (3 H, s, 7-OMe), 3.78 (3 H, s, 4′-OMe), and 6.5—7.0 (4 H, 4 d, *J* 8 Hz, 5-H, 5′-H, 6-H, 6′-H); δ_C 14.3 (3′-Me), 17.8, 18.3 (7′-Me, 4-Me), 26.4 (1-Me), 29.9 (C-3), 39.9 (C-2), 41.9 (C-1′), 49.7 (C-1), 55.6, 55.3 (4′-OMe, 7-OMe), 109.2, 109.5 (C-5′, C-6), 124.8 (C-7a), 125.1 (C-6′), 125.7 (C-3a′), 128.3 (C-5), 132.2 (C-7′), 135.2 (C-4), 138.0 (C-3′), 142.8 (C-7a′), 143.2 (C-3a), 147.4 (C-2′), 152.6 (C-4′), and 154.6 (C-7); *m*/*z* 348 (M^+ 50%), 175 (100). The methanol-soluble material from the preparation of the dimer (**15**) was recovered by dilution with water and ether extraction. The resulting oil (540 mg) was separated by p.l.c. to give the indene (**5**) (190 mg) and a compound tentatively identified from spectral data as 3-(2′,3′-dihydro-1′,4′-dimethyl-7′-methoxy-1*H*-indenylmethyl)-4-methoxy-7-methyl-1*H*-indene (**17**) (90 mg); δ_H ($CDCl_3$) 1.46 (3 H, s, 1′-Me), 2.16 (3 H, s, 4′-Me), 2.24 (3 H, s, 7-Me), 2.5—2.8 (4 H, m, 2′-H_2, 3′-H_2), 3.02 (2 H, m, $W_{\frac{1}{2}}$ 5 Hz, 1-H_2), 3.1—3.4 (2 H, m, 3-CH_2), 3.76 and 3.82 (2 × 3 H, 2 s, 4-OMe, 7′-OMe), 6.5—7.0 (4 H, 4 d, *J* 8 Hz, 4-H, 6-H, 5′-H, 6′-H), and 5.75 (1 H, m, 2-H); δ_C 17.8 and 18.2 (4′-Me, 7-Me), 26.4 (1′-Me), 29.7 (C-3′), 37.1, 37.36, and 37.43 (C-1, C-2′, 3-CH_2), 50.2 (C-1′), 55.0 (4-OMe, 7′-OMe), 108.8 and 109.1 (C-5, C-6′), 125.1 and 125.5 (C-3a, C-7a′), 133.8 (C-4), 137.5 (C-4′), 142.6 (C-3a′), 144.4 and 145.0 (C-3, C-7a), 152.9 (C-4), and 155.1 (C-7′); *m*/*z* 348 (M^+, 18%), 175 (100), and 174 (70).

2,3-*Dihydro*-7-*hydroxy*-3,4-*dimethyl*-1H-*indan*-1-*one* (**7**).—The indanone (**7**)[1] was purified by sublimation and crystallisation, m.p. 52—54 °C (from hexane) (lit.,[7] 53 °C); $\nu_{max.}$ (CCl_4) 3 330 (OH) and 1 680 cm^{-1} (CO); δ_H ($CDCl_3$) 1.30 (3 H, d, *J* 7 Hz, 3-Me), 2.26 (1 H, dd, *J* 23 Hz and 2 Hz, 2β-H), 2.30 (3 H, s, 4-Me), 3.0 (1 H, dd, *J* 23 Hz and 7 Hz, 2α-H), 3.46 (1 H, dd, *J* 7 Hz and 2 Hz, 3α-H), 6.70 (1 H, d, *J* 8 Hz, 6-H), 7.26 (1 H, d, *J* 8 Hz, 5-H), and 9.0 (1 H, s, exch. on deuteriation, 7-OH).

2,3-*Dihydro*-1,3,4-*trimethyl*-1H-*indene*-1,7-*diol* (**9**, **10**).[1]—The ketone (**7**) (1 g, 5.8 mmol) in ether (6 ml) was added slowly to a stirred solution of methylmagnesium iodide (20 mmol) in ether (10 ml) under nitrogen and cooled on ice. The mixture was then heated under reflux for 1 h, cooled, and triethylamine (2.5 g, 25 mmol) was added. The mixture was cautiously added to well stirred ether (100 ml) and aqueous KH_2PO_4 (0.5 mol l^{-1})–K_2HPO_4 (0.5 mol l^{-1}) buffer (200 ml). Work-up gave the crude product (**9**), (**10**) (0.94 g, 86%) which consisted of a mixture (2:1) of alcohol diastereoisomers and starting material (*ca.* 10%). The major product (**10**) underwent elimination readily while the minor isomer (**9**) was enriched by crystallisation from pentane; δ_H (**10**) ($CDCl_3$) 1.28 (3 H, d, *J* 7 Hz, 3-Me), 1.52 (3 H, s, 1-Me), 2.20 (3 H, s, 4-Me), 6.56 (1 H, d, *J* 8 Hz), and 6.90 (1 H, d, *J* 8 Hz, 5-H); (**9**)[1] 1.22 (3 H, d, *J* 7 Hz, 3-Me), 1.69 (3 H, s, 1-Me), 2.17 (3 H, s, 4-Me), 1.88 (1 H, dd, *J* 13 Hz and 1.5 Hz, 2α-H), 2.43 (1 H, br d, *J* 13 Hz, $W_{\frac{1}{2}}$ 3 Hz, 2β-H), 3.20 (1 H, br q, *J* 7 Hz, $W_{\frac{1}{2}}$ 4.5 Hz, 3β-H), 6.56 (1 H, d, *J* 8 Hz, 6-H), 6.90 (1 H, d, *J* 8 Hz, 5-H), and 7.0 (2 H, br s, 1-OH, 7-OH); *m*/*z* 192 (M^+, 2%) and 174 (100).

1,3,7-*Trimethyl*-1H-*inden*-4-*ol* (**2**).—The crude mixture of diols (**9**), (**10**) (0.5 g, 0.26 mmol) in acetonitrile (10 ml) was mixed with trifluoroacetic acid (0.05 ml) in acetonitrile (10 ml). After 20 min, an excess of aqueous sodium hydrogen carbonate was added, and work-up gave the crude indene (**2**) (0.44 g, 0.26 mmol). Sublimation (60 °C at 0.3 mmHg) gave crystals, m.p. 96—100 °C (0.38 g, 85%). Further purification gave the *indene* (**2**), m.p. 101—102.5 °C (from hexane) (Found: C, 83.1; H, 8.2. $C_{12}H_{14}O$ requires C, 82.7; H, 8.1%); δ_H ($CDCl_3$) 1.22 (3 H, d, *J* 7.4 Hz, 1-Me), 2.30 (3 H, t, *J* 1.5 Hz, 3-Me), 2.33 (3 H, s, 7-Me), 3.40 (1 H, m, 1-H), 5.92 (1 H, m, 2-H), 6.50 (1 H, d, *J* 8.5 Hz, 5-H), 6.80 (1 H, d, *J* 8.5 Hz, 6-H), and 4.8 (1 H, br s, exchanges on deuteriation, 4-OH); *m*/*z* 174 (M^+ 100%).

(1β, 3β)-2,3-*Dihydro*-1,3,7-*trimethyl*-1H-*inden*-4-*ol* (**41**).—The indene (**2**) (135 mg) in ethyl acetate (10 ml) was stirred with 10% palladium on charcoal (10 mg) under an atmosphere of hydrogen for 2 h to give the indan which was sublimed (60 °C at 0.3 mmHg), m.p. 80—83 °C (lit.,[1] 83.5—84 °C); δ_H ($CDCl_3$) 1.28 (3 H, d, *J* 7 Hz, 1-Me), 1.36 (3 H, d, *J* 7 Hz, 3-Me), 1.42 (1 H, dt, *J* 12 Hz and 1.8 Hz, 2β-H), 2.22 (3 H, s, 7-Me), 2.50 (1 H, dt, *J* 12 Hz, and 9 Hz, 2α-H), 3.2 (2 H, m, 1-H, 3-H), 4.8 (1 H, br s, (4-OH), 6.48 (1 H, d, *J* 8 Hz, 5-H), and 6.86 (1 H, d, *J* 8 Hz, 6-H).

[6a-$^{13}CH_3$, 11b-$^{13}CH_3$]-*Dimers* (**25**) *and* (**26**).—Butyl-lithium in hexane (1.6 mol l^{-1}, 0.6 ml, 0.95 mmol) was added to a stirred and cooled (0 °C) solution of the ketone (**7**) (0.167 g, 0.95 mmol) in ether (2 ml). The resulting yellow solution was added to [$^{13}C_1$]methylmagnesium iodide [prepared from 97% [^{13}C]methyl iodide (0.142 g, 1 mmol) and magnesium (0.04 g, 1.6 mmol)] in ether (0.5 ml) and the mixture was heated under reflux for 2 h. Aqueous acetic acid (1 mol l^{-1})–sodium acetate (1 mol l^{-1}) (2 ml) was added to the cooled mixture and work-up gave crude product (0.16 g) which contained (^1H n.m.r.) a mixture (2:3) (*ca.* 50%) of the [1-$^{13}CH_3$]alcohols (**9**) and (**10**), starting material (**7**) (*ca.* 20%), and the 1-butyl alcohol (**40**) (*ca.* 30%); δ_H as for mixture of (**9**), (**10**), (**7**), and (**40**) except: 1.52 [d, *J* 126 Hz, 1-$^{13}CH_3$-(**10**)], 1.69 [d, *J* 126 Hz, 1-$^{13}CH_3$-(**9**)]. The crude mixture was dissolved in ether (2 ml) and stirred vigorously with aqueous sulphuric acid (2 mol l^{-1}; 10 ml) for 2 h. Work-up and p.l.c. gave a mixture (*ca.* 1:3) (0.06 g) of the butylindene (**4**) and [3-$^{13}CH_3$]indene (**2**); δ_H as for a mixture of (**4**) and (**2**) except 2.30 [dt, *J* 126 Hz and 1.5 Hz, 3-$^{13}CH_3$-(**2**)]; *m*/*z* 216 [M^+, (**4**), 7%] and 175 [M^+, 3-$^{13}CH_3$-(**2**), 100]. The mixture was dissolved in deuteriochloroform (0.4 ml) and a solution of trifluoroacetic acid in tetrachloromethane (5% v/v; 0.02 ml) was added. After 10 min the solution contained (*ca.* 60%) the [6a-$^{13}CH_3$, 11b-$^{13}CH_3$]-dimer (**23**), δ_H 1.53 (d, *J* 126 Hz, 11b-$^{13}CH_3$), 2.01 (d, *J* 126 Hz, 6a-$^{13}CH_3$). Trifluoroacetic acid (0.02 ml) was then added to the solution and after 5 min a mixture (2:1) of the (6a-$^{13}CH_3$, 11b-$^{13}CH_3$)-dimer (**25**) and the dimer (**34**) was produced; δ_H 0.92 [d, *J* 126 Hz, 11b-$^{13}CH_3$-(**25**)], 1.63 [d, *J* 126 Hz, 6a-$^{13}CH_3$-(**25**)], and 0.99 [d, *J* 126 Hz, 11b-$^{13}CH_3$-(**37**)]. After 4 h the mixture contained (6a-$^{13}CH_3$, 11b-$^{13}CH_3$)-dimers (**25**) and (**26**) and crossed dimers (**34**) and (**35**) (2:2:1:1). Work-up and p.l.c. gave (i) a mixture (1:1) of the (6a-$^{13}CH_3$, 11b-$^{13}CH_3$) dimers (**25**) and (**26**) (0.02 g); δ_H as for a mixture (1:1) of dimers (**25**) and (**26**) except that the 6a- and 11b-methyl signals showed 126 Hz coupling; δ_C 18.8 [(11b-$^{13}CH_3$)-(**26**)], 21.8 [(11b-$^{13}CH_3$)-(**25**)], 30.2 [(6a-$^{13}CH_3$)-(**25**)], and 30.4 [(6a-$^{13}CH_3$)-(**26**)]; *m*/*z* 250 (M^+ 10%), 175 (100); (ii) a mixture (1:1) of crossed dimers (**34**) and (**35**) (10 mg); δ_H 0.79 [d, *J* 126 Hz, 11b-$^{13}CH_3$-(**32**)], 0.88 [d, *J* 126 Hz, 11b-$^{13}CH_3$-(**31**)], 1.30, 1.33 (2 d, *J* 7 Hz, 2-Me, 11-Me), 0.9—2.4 (butyl protons), 2.26 (s, 3-Me, 10-Me), 3.30 (m, 2-H, 11-H), 6.4—6.9 (ArH, OH); δ_C 19.2 [(11b-$^{13}CH_3$)-(**35**)], 22.3 [(11b-$^{13}CH_3$)-(**34**)]; *m*/*z* 391 (M^+, 2%), 216 (78), 176 (85), and 175 (100).

A mixture of (6a-$^{13}CH_3$, 11b-$^{13}CH_3$)-dimers (**25**) and (**26**) (15 mg) and unlabelled dimer (**25**) (15 mg) was dissolved in chloroform and the solvent was removed to give a homogeneous solid; *m*/*z* 250 (3%), 248 (2), 176 (64), 175 (100), 174 (53), 160 (36), and 159 (50). The mixture was redissolved in deuteriochloroform (0.4 ml) containing trifluoroacetic acid (0.02 ml). The solution was added to aqueous sodium hydrogen carbonate after 2.5 h and work-up gave a mixture (1:1) of dimers (**25**) and (**26**) with redistributed ^{13}C labels; *m*/*z* 350 (2%), 349 (3), 348 (2), 176 (59), 175 (100), 174 (47), 160 (31), and 150 (43).

(2β,6aβ,11β,11aβ,11bα)-8-*Bromo*-1,2,6a,11,11a,11b-*hexahydro*-2,3,6a,10,11,11b-*hexamethyldi-indeno*[7,1-bc:2′,1′-e]*pyran*-7-*ol* (**27**).—A mixture (1:1) of dimer (**25**) and dimer (**26**) (0.25 g, 0.72 mmol) in dioxane (15 ml) and water (2.5 ml) was reacted with bromine in dioxane (0.2 mol l^{-1}, 4 ml, 0.8 mmol) for 5 min. Work-up and p.l.c. gave a mixture (0.25 g, 90%) which was purified by repeated fractional crystallisation to give bromo-dimer (**27**), m.p. 189—191 °C (from pentane then dichloromethane) (lit.,[1] 178—180 °C); δ_C 17.3 (10-Me), 18.8 (3-Me, 11b-Me), 19.9 (2-Me), 20.8 (11-Me), 30.2 (6a-Me), 38.4 (C-2), 39.3 (C-11), 42.1 (C-11b), 51.8 (C-1), 68.0 (C-11a), 92.3 (C-6a), 107.9 (C-8), 114.4 (C-5), 126.5 (C-6b), 128.0 (C-11c), 130.1 (C-4), 131.5 (C-10), 134.2 (C-9), 137.2 (C-3), 143.5 (C-2a), 144.4 (C-10a), 147.5 (C-7), and 148.4 (C-5a); *m*/*z* 428, 426 (M^+ 7%), 254, 252 (20), 175 (100), and 174 (86).

(2α,6aβ,11β,11aβ,11bα)-8-*Bromo*-1,2,6a,11,11a,11b-*hexahydro*-2,3,6a,10,11,11b-*hexamethyldi-indeno*[7,1-bc:2′,1′-e]-*pyran*-7-*ol* (**28**).—Dimer (**25**) was treated with bromine as described above. Recrystallisation of the crude product gave the *bromo derivative* (**28**), m.p. 166—169 °C (from pentane then dichloromethane); δ_C 17.3 and 17.7 (3-Me, 10-Me), 20.8 (11-Me), 21.7, 21.8 (2-Me, 11b-Me), 29.9 (6a-Me), 38.6 (C-2), 39.3 (C-11), 43.6 (C-11b), 49.2 (C-1), 68.4 (C-11a), 92.5 (C-6a), 107.9 (C-8), 115.1 (C-5), 126.5 (C-6b), 127.8 (C-11c), 129.5 (C-4), 131.5 (C-10), 134.2 (C-9), 137.1 (C-3), 144.5 (C-2a), 144.9 (C-10a), 147.9 (C-7), and 148.7 (C-5a); *m*/*z* 428, 426 (M^+), 254, 252, 175, and 174.

3-*Butyl*-7-*methyl*-1H-*inden*-4-*ol* (**3**).—Butyl-lithium (1.5 mol l^{-1} in hexane; 2 ml, 3 mmol) was added to the ketone (**6**) (120 mg, 0.74 mmol) in ether (3 ml). The mixture was stirred and heated under reflux for 2 h then cooled and added slowly to acetic acid (1 mol l^{-1})–sodium acetate (1 mol l^{-1}) buffer. Ether extraction and work-up gave crude alcohol (160 mg) which was dissolved in methanol (10 ml) and ether (5 ml), and aqueous sulphuric acid (2 mol l^{-1}; 2 ml) was added. Work-up after 30 min gave the crude product (140 mg) which was purified by p.l.c. and sublimation to give the *indene* (**3**) (90 mg, 60%), m.p. 62—65.5 °C (Found: C, 83.1; H, 9.2. $C_{14}H_{18}O$ requires C, 83.1; H, 9.0%); δ_H ($CDCl_3$) 0.8—1.8 (7 H, m, $CH_2CH_2CH_3$), 2.24 (3 H, s, 7-Me), 2.6—2.9 (2 H, m, 3-CH_2), 3.16 (2 H, m, $W_{\frac{1}{2}}$ 5 Hz, 1-H_2), 4.9 (1 H, br s, 4-OH), 6.02 (1 H, m, $W_{\frac{1}{2}}$ 5 Hz, 2-H), 6.52 (1 H, d, *J* 8.5 Hz, 5-H), and 6.82 (1 H, d, *J* 8.5 Hz, 6-H). P.l.c. also yielded (E)-1-*butylidene*-2,3-*dihydro*-4-*methylinden*-7-*ol* (**11**) (15%), m.p. 112.5—114.5 °C (from hexane) (Found: C, 83.2; H, 8.95. $C_{14}H_{18}O$ requires C, 83.1; H, 9.0%); δ_H (CCl_4) 0.8—2.3 (7 H, m, $CH_2CH_2CH_3$), 2.12 (3 H, s, 4-Me), 2.66 (4 H, br s, $W_{\frac{1}{2}}$ 5 Hz, 2-H_2, 3-H_2), 4.8 (1 H, br s, 7-OH), 6.04 (1 H, tt, *J* 7 Hz and 2 Hz, 1′ =C-H), 6.22 (1 H, d, *J* 8 Hz, 6-H), and 6.56 (1 H, d, *J* 8 Hz, 5-H); δ_C 14.0 (C-4′), 17.9 (4-Me), 22.8 (C-3′), 28.2, 29.2 (C-2, C-3), 32.2 (C-2′), 113.8 (C-6), 123.7 (C-1′), 126.1 (C-7a), 127.4 (C-4), 128.2 (C-5), 141.8 (C-1), 146.9 (C-3a), and 150.5 (C-7); *m*/*z* (12 eV) 202 (M^+, 100%), 174 (11), (70 eV) 202 (M^+, 35), and 173 (100).

(2α,6aβ,11aβ,11bα)- *and* (2β,6aβ,11aβ,11bα)-6a-*Butyl*-1,2,6a,11,11a,11b-*hexahydro*-2,3,10,11b-*tetramethyldi-indeno*-[7,1-bc:2′,1′-e]*pyran*-7-*ol* (**34**) *and* (**35**).—Trifluoroacetic acid (0.5 ml) was added to a mixture of indenes (**3**) (50 mg) and (**2**) (170 mg) in chloroform (15 ml). The solution was heated under reflux for 1 h. Work-up and p.l.c. gave a mixture (1:1) of dimers (**25**) and (**26**) (80 mg), and a mixture (1:1) of crossed dimers (**34**) and (**35**) (70 mg); δ_H ($CDCl_3$) 0.66 [s, 11b-Me of (**35**)] and 0.86 [s, 11b-Me of (**34**)]; *m/z* (12 eV) 376 (M^+, 6%), 202 (60), 175 (100), 174 (98), 160 (67), 159 (30), (70 eV) 376 (M^+, 3), 202 (18), 175 (100), 160 (58), and 159 (60).

3-*Butyl*-1,7-*dimethyl*-1H-*inden*-4-*ol* (**4**).—Butyl-lithium (1.5 mol l^{-1} in hexane; 5.7 ml, 8.5 mmol) was added to the ketone (**7**) (0.50 g, 2.8 mmol) in ether (5 ml) cooled in ice. The mixture was stirred and heated under reflux for 1 h and then added to a well-stirred mixture of aqueous acetic acid (1 mol l^{-1})–sodium acetate (1 mol l^{-1}) buffer (50 ml), ice, and ether (50 ml). Work-up gave the crude product (0.65 g) which was dissolved in methanol (20 ml) and ether (10 ml). Dilute sulphuric acid (2 mol l^{-1}; 1 ml) was added and the solution was stirred at room temperature for 30 min. Work-up and p.l.c. gave the *indene* (**4**) (0.285 g, 47%), m.p. 53.5—55.5 °C (from hexane) (Found: C, 83.5; H, 9.5. $C_{15}H_{20}O$ requires C, 83.3; H, 9.3%); δ_H ($CDCl_3$) 0.95 (3 H, m, butyl-Me), 1.24 (3 H, d, *J* 7 Hz, 1-Me), 1.3—1.8 (4 H, m, CH_2CH_2), 2.30 (3 H, s, 7-Me), 2.5—2.85 (2 H, m, 3-CH_2), 3.1—3.6 (1 H, m, 1-H), 4.7 (1 H, br s, 4-OH), 5.92 (1 H, m, $W_{\frac{1}{2}}$ 4 Hz, 2-H), 6.46 (1 H, d, *J* 8 Hz, 5-H), and 6.78 (1 H, d, *J* 8 Hz, 6-H).

(6aβ, 11β, 11aβ,11bα)-6a-*Butyl*-1,2,6a,11,11a,11b-*hexahydro*-3,10,11,11b-*tetramethyldi-indeno*[7,1-bc:2′,1′-e]*pyran*-7-*ol* (**33**).—A solution of trifluoroacetic acid in tetrachloromethane (5% v/v; 0.5 ml) was added to a mixture of indenes (**4**) (0.50 g) and (**2**) (0.50 g) in chloroform (20 ml). Additional trifluoroacetic acid (0.5 ml) was added after 15 min and the mixture was left for a further 15 min. Work-up and p.l.c. gave the *crossed dimer* (**33**) (0.20 g, 23%), m.p. 119—120.5 °C (from hexane) (Found: C, 83.0; H, 8.8. $C_{26}H_{32}O_2$ requires C, 82.9; H, 8.6%); δ_H ($CDCl_3$) 1.70 (3 H, s, 11b-Me), 1.0—2.2 (12 H, m, butyl H, 1-H_2, 11a-H), 1.40 (3 H, d, *J* 7.5 Hz, 11-Me), 2.18, 2.24 (2 × 3 H, 2 s, 3-Me, 10-Me), 2.65—3.0 (2 H, m, 2-H_2), 3.36 (1 H, br q, *J* 7.5 Hz, 11-H), 6.5—7.05 (4 H, 4 d, *J* 8.5 Hz, 4-H, 5-H, 8-H, 9-H), and 7.4 (1 H, br s, 7-OH); *m/z* (12 eV) 376 (M^+, 7%), 216 (100), 174 (20), 161 (51), 160 (40), (70 eV) 376 (M^+ 2), 216 (28), 174 (26), and 161 (100); δ_C – not included in Table 1 are 13.9 (C-4′), 23.0 (C-3′), 26.2 (C-2′), and 44.9 (C-1′).

(6aβ,11β,11aβ,11bα)-8-*Bromo*-6a-*butyl*-1,2,6a,11,11a,11b-*hexahydro*-3,10,11,11b-*tetramethyldi-indeno*[7,1-bc:2′,1′-e]-*pyran*-7-*ol* (**38**).—Bromine (60 mg, 0.38 mmol) in dioxane (2 ml) was added to the crossed dimer (**33**) (140 mg, 0.37 mmol) in water (0.8 ml) and dioxane (5 ml). After 5 min, aqueous sodium sulphite and sodium hydrogen carbonate were added. Work-up and p.l.c. gave the 8-*bromo derivative* (**38**), m.p. 142—143 °C (from hexane) (Found: C, 68.6; H, 6.8; Br, 18.3. $C_{26}H_{31}BrO_2$ requires C, 68.6; H, 6.9; Br, 17.55%); δ_H ($CDCl_3$) 1.70 (3 H, s, 11b-Me), 1.0—2.2 (12 H, m, butyl H, 1-H_2, 11a-H), 1.40 (3 H, d, 11-Me), 2.18, 2.22 (2 × 3 H, 2 s, 3-Me, 10-Me), 2.65—3.0 (2 H, m, 2-H_2), 3.0—3.5 (1 H, m, 11-H), 6.58 (1 H, d, *J* 8 Hz, 5-H), 6.86 (1 H, d, *J* 8 Hz, 4-H), 7.16 (1 H, s, 9-H), and 7.3 (1 H, s, 7-OH); *m/z* 456, 454 (M^+, <1%), 296, 294 (7), and 161 (100).

(6aβ,11aβ,11bβ)-11b-*Butyl*-1,2,6a,11,11a,11b-*hexahydro*-3,-6a,10-*trimethyl-di-indeno*[7,1-bc:2′,1′-e]*pyran*-7-*ol* (**29**).—A solution of trifluoroacetic acid in tetrachloromethane (5% v/v; 0.25 ml) was added to a mixture of the indenes (**1**) (100 mg) and (**3**) (150 mg) in chloroform (5 ml). The solution was left at room temperature for 90 min. Work-up and p.l.c. gave the *crossed dimer* (**29**) (60 mg) as a viscous oil (Found: M^+, 362.2234. $C_{25}H_{30}O_2$ requires M^+ 362.2246); δ_H (CCl_4) 0.9—1.9 (11 H, m, butyl H, 1-H_2), 1.92 (3 H, s, 6a-Me), 2.02 and 2.10 (2 × 3 H, 2 s, 3-Me, 10-Me), 2.1—3.2 (5 H, m, 2-H_2, 11-H_2, 11a-H), 6.0 (1 H, br s, 7-OH), and 6.4—6.8 (4 H, 4d, *J* 8 Hz, 4-H, 5-H, 8-H, 9-H); *m/z* (12 eV) 362 (M^+, 5%), 204 (60), 203 (91), 160 (100); (70 eV) 362 (4), 203 (78), 173 (100), 160 (84), and 145 (86); not included in Table 1 are δ_C 14.1 (C-4′), 23.3 (C-3′), 27.2 (C-2′), and 38.5 (C-1′).

(6aβ,11aβ,11bβ)-8-*Bromo*-11b-*butyl*-1,2,6a,11,11a,11b,-*hexahydro*-3,6a,10-*trimethyldi-indeno*[7,1-bc:2′,1′-e]*pyran*-7-*ol* (**32**).—Bromine (30 mg, 0.2 mmol) in dioxane (3 ml) was added to the crossed dimer (**29**) (35 mg, 0.1 mmol) in dioxane (2 ml) containing 5% aqueous sodium hydrogen carbonate (0.5 ml). After 5 min a solution of sodium sulphite in 5% aqueous sodium carbonate was added. Work-up and p.l.c. gave the 8-*bromo-derivative* (**32**) (0.35 g, 82%), m.p. 156—157.5 °C (from pentane) (Found: C, 67.9; H, 6.5; Br, 18.9. $C_{25}H_{29}BrO_2$ requires C, 68.0; H, 6.6, Br, 18.1%); δ_H 0.9—1.9 (11 H, m, butyl H, 1-H_2), 1.96, 2.00 and 2.12 (3 × 3 H, 3 s, 3-Me, 6a-Me, 10-Me), 2.1—3.2 (5 H, m, 2-H_2, 11-H_2, 11a-H), 6.1 (1 H, br s, 7-OH), 6.42 (1 H, d, *J* 8.5 Hz, 4-H), 6.70 (1 H, d, *J* 8.5 Hz, 5-H), and 7.02 (1 H, s, 9-H); *m/z* (12 eV) 442, 440 (M^+, 1%), 240, 238 (49), 203 (100), 202 (87), 175 (48), 159 (48); (70 eV) 442, 440 (<1), 240, 238 (17), 203 (81), 175 (100), and 159 (79).

(6aβ,11aβ,11bα)-11b-*Butyl*-1,2,6a,11,11a,11b-*Hexahydro*-3,-6,10-*trimethyldi-indeno*[7,1-bc:2′,1′-e]*pyran*-7-*ol* (**30**).—During the purification of the crossed dimer (**37**) by p.l.c. a fraction of lower R_F was recovered which contained dimers (**12**) and (**30**). Repeated p.l.c. allowed isolation of a small amount (*ca.* 4 mg) of the crossed dimer (**30**), m.p. 108—115 °C (Found: M^+, 362.2231. $C_{25}H_{30}O_2$ requires M^+, 362.2245); δ_H (CCl_4) 1.46 (6a-Me) and 2.16 (3-Me, 10-Me); *m/z* (70 eV) 362 (M^+, 4%), 203 (88), 173 (73), 160 (100), 147 (77), and 145 (80).

(2β,6aβ,11aβ,11bβ)-11b-*Butyl*-1,2,6a,11,11a,11b-*hexahydro*-2,3,6a,10-*tetramethyldi-indeno*[7,1-bc:2′,1′-e]*pyran*-7-*ol* (**31**).—A solution of trifluoroacetic acid in tetrachloromethane (5% v/v; 0.25 ml) was added to a mixture of the indenes (**1**) (80 mg) and (**4**) (160 mg) in chloroform (5 ml). After 90 min, work-up and p.l.c. gave the crossed dimer (**31**) (45 mg) as a viscous oil (Found: M^+, 376.2388. $C_{26}H_{32}O_2$ requires *M*, 376.2402); δ_H ($CDCl_3$) 0.8—2.4 (12 H, m, butyl H, 1-H_2, 11a-H), 1.38 (3 H, d, *J* 7 Hz, 2-Me), 1.92 (3 H, s, 6a-Me), 2.00 (3 H, s, 10-Me), 2.20 (3 H, s, 3-Me), 2.5—3.4 (3 H, m, 2-H, 11-H_2), 6.0 (1 H, br s, 7-OH), and 6.4—6.9 (4 H, 4 d, *J* 8 Hz, 4-H, 4-H, 8-H, 9-H); *m*/z (12 eV) 376 (M^+, 1%), 217 (100), 187 (20), and 160 (63); δ_C – not included in Table 1, 14.1 (C-4′), 23.3 (C-3′), 27.3 (C-2′), and 41.8 (C-1′).

Dehydration of 2,3-*Dihydro*-1,4-*dimethyl*-1H-*indene*-1,7-*diol* (**8**).—A mixture (*ca.* 6:1) (2.7 g) of the alcohol (**8**) and the ketone (**1**) was dissolved in methanol and concentrated under reduced pressure to leave an oil which was stored overnight; the remaining solvent was then removed under high vacuum. After several days at room temperature the now solid mixture was melted on a hot-water bath and then left for a further 5 days at room temperature with occasional warming to melt any crystalline material. The complex product mixture was chromatographed on silica gel S (350 g) using hexane–ether (9:1) as eluant to give, in order of elution (i) dimer (**12**) (trace); (ii) (2*R**,3a*R**)-2′,3,3′,3a,4,5-*hexahydro*-3a,4′,6-*trimethylspiro*-(*cyclopenta*[de]-1-*benzopyran*-2,1′-*inden*)-7′-*ol* (**18**) (0.38 g), m.p. 146—148.5 °C (from hexane–ether) (Found: C, 82.45; H, 7.8. $C_{22}H_{24}O_2$ requires C, 82.5; H, 7.55%); δ_H ($CDCl_3$) 1.27 (3 H, s, 3a-Me), 2.16, 2.25 (2 × 3 H, 2 s, 4′-Me, 6-Me), 1.7—3.1 (10

H, m, 3-H_2, 2′-H_2, 3′-H_2, 4-H_2, 5-H_2), 6.4 (1 H, s, 7′-OH), 6.64, 6.70 (2 H, 2 d, *J* 8.5 Hz, 5′-H, 7-H), and 6.88, 6.98 (2 H, 2 d, *J* 8.5 Hz, 6′-H, 8-H); δ_C 17.6, 18.2 (4′-Me, 6-Me), 27.9, 29.4 (C-3′, C-5), 29.0 (3a-Me), 39.2 (C-3), 39.7 (C-3a), 44.4 (C-4), 47.9 (C-2′), 92.9 (C-2), 114.4, 115.8 (C-6′, C-8), 125.5 (C-7a′), 128.2 (C-7, C-8b), 130.6 (C-4′, C-5′), 139.2 (C-6), 141.1 (C-3a′, C-5a), 149.7 (C-8a), and 150.5 (C-7′); *m/z* (12 eV) 320 (M^+, 12%), 161 (85), and 160 (100); (iii) (2*R**,3a*S**)-2′,3,3′,3a,4,5-*hexahydro*-3a,4′,6-*trimethylspiro*(*cyclopenta*[de]-1-*benzopyran*-2,1′-*inden*)-7′-*ol* (**19**) (0.46 g), m.p. 143—147.5 °C (from hexane–ether) (Found: C, 82.6; H, 7.6. $C_{22}H_{24}O_2$ requires C, 82.5; H, 7.55%); δ_H ($CDCl_3$) 1.38 (3 H, s, 3a-Me), 2.18 (6 H, s, 4′-Me, 6-Me), 1.9—3.2 (10 H, m, 2′-H_2, 3-H_2, 3′-H_2, 4-H_2, 5-H_2), 4.8 (1 H, s, 7′-OH), 6.54 and 6.60 (2 H, 2 d, *J* 8.5 Hz, 5′-H, 7-H), and 6.92 and 6.96 (2 H, 2 d, *J* 8.5 Hz, 6′-H, 8-H); δ_C 17.8 and 18.0 (4′-Me, 6-Me), 24.0 (3a-Me), 28.5, 29.0 (C-3′, C-5), 40.1 (C-3, C-3a), 43.8 and 44.8 (C-4, C-2′), 91.1 (C-2), 112.6 and 114.8 (C-8, C-6′), 125.7 and 126.3 (C-7a′, C-8b), 129.6 and 130.4 (C-5′, C-7), 132.2 and 133.9 (C-4′, C-6), 141.8 and 141.9 (C-3a′, C-5a), 149.2 (C-8a), and 150.2 (C-7′); *m/z* (12 eV) 320 (M^+, 20%), 161 (90), and 160 (100); (iv) indene (**1**) (0.40 g); (v) a mixture of dimers (**13**), (**14**), and (**16**) (0.47 g); (vi) ketone (**6**) (0.33 g). Elution with ether gave a complex mixture of polar material (0.28 g).

(6aβ,11aβ,11bα)-6a-*Butyl*-1,2,6a,11,11a,11b-*hexahydro*-3,-10,11b-*trimethyldi-indeno*[7,1-bc:2′,1′-e]*pyran*-7-*ol* (**37**).—The spiro-indene (**19**) (400 mg) and the mixture of dimers derived from indene (**3**) (500 mg) were dissolved in chloroform to which trifluoroacetic acid (0.1 ml) had been added. After 36 h at room temperature, work-up and p.l.c. yielded the *crossed dimer* (**37**) (110 mg) as a viscous oil (Found: C, 83.1; H, 8.5. $C_{22}H_{30}O_2$ requires C, 82.8; H, 8.3%); δ_H (CCl_4) 0.68 (3 H, s, 11b-Me), 0.7—2.5 (12 H, m, butyl H, 1-H_2, 11a-H), 2.20 (6 H, s, 3-Me, 10-Me), 2.6—3.0 (4 H, m, 2-H_2, 11-H_2), 6.5—7.0 (4 H, 4 d, *J* 8 Hz, 4-H, 5-H, 8-H, 9-H), and 6.5 (1 H, s, 7-OH); *m/z* 362 (M^+, 2%), 202 (20), 161 (100), 160 (80), and 145 (19); not included in Table 1 are δ_C 13.9 (C-4′), 22.9 (C-3′), 26.1 (C-2′), and 41.6 (C-1′).

3-(2′,3′-*Dihydro*-1′,4′-*dimethyl*-7′-*hydroxy*-1′H-*indenylmethyl*)-7-*methyl*-1H-*inden*-4-*ol* (**16**).—Trifluoroacetic acid (0.01 ml) was added to a mixture of dimers (**18**) and (**19**) (0.13 g) in dichloromethane (1.5 ml) and methanol (3 ml). After 90 s, excess of aqueous sodium hydrogen carbonate was added, and work-up and p.l.c. gave the uncyclised dimer (**16**) (0.11 g, 85%) as a viscous oil; δ_H ($CDCl_3$) 1.38 (3 H, s, 1′-Me), 2.14 and 2.22 (2 × 3 H, 2 s, 4′-Me, 7-Me), 1.7—3.7 (8 H, m, 1-H_2, 3-H_2, 2′-H_2, 3′-H_2), 6.16 (1 H, m, $W_{\frac{1}{2}}$ 5 Hz, 2-H), 6.4 (2 H, br s, 4-OH, 7′-OH), 6.62 (2 H, d, *J* 8.5 Hz, 6-H, 5′-H), and 6.86 and 6.94 (2 H, 2 d, *J* 8.5 Hz, 5-H, 6′-H); δ_C 17.8 and 18.2 (7-Me, 4′-Me), 24.0 (1′-Me), 29.1 (C-3′), 37.0, 37.3, and 39.7 (C-1, C-2′, 3-CH_2), 48.6 (C-1′), 114.5 and 114.7 (C-5, C-6′), 125.7 and 126.2 (C-3a, C-7a′), 126.7 (C-6), 128.9 (C-5′), 129.3 (C-2), 132.0 and 135.6 (C-7, C-4′), 141.6 (C-3), 143.8 and 145.2 (C-3a′, C-7a), and 147.7 and 149.9 (C-7′, C-4); *m/z* (12 eV) 320 (M^+, 5%), 318 (14), 161 (93), and 160 (100). A fraction (10 mg) of lower R_F was tentatively identified as 1-(2′,3′-dihydro-1′,4′-dimethyl-7′-hydroxy-1*H*-indenylmethylene)-2,3-dihydro-4-methylinden-7-ol (**21**); δ_H (CCl_4) 1.38 (3 H, s, 1′-Me), 2.18 and 2.27 (2 × 3 H, 2 s, 4-Me, 4′-Me), 2.0—3.0 (8 H, m, 2-H_2, 2′-H_2, 3-H_2, 3′-H_2), 5.2 (2 H, br s, 7-OH, 7′-OH), and 6.2—6.9 (5 H, arom. H, 1 =CH–). This compound isomerised overnight to a mixture shown (^{1}H n.m.r., t.l.c.) to contain dimers (**18**), (**19**), and (**16**).

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