A Novel Chiral Approach to *trans*-3a,4,5,9b-Tetrahydro-1*H*-benz[*e*]indene[1]

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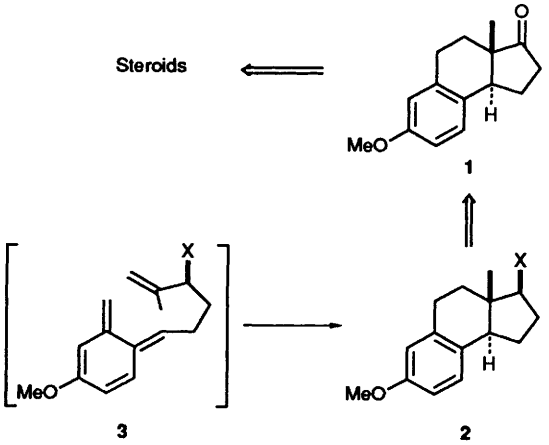
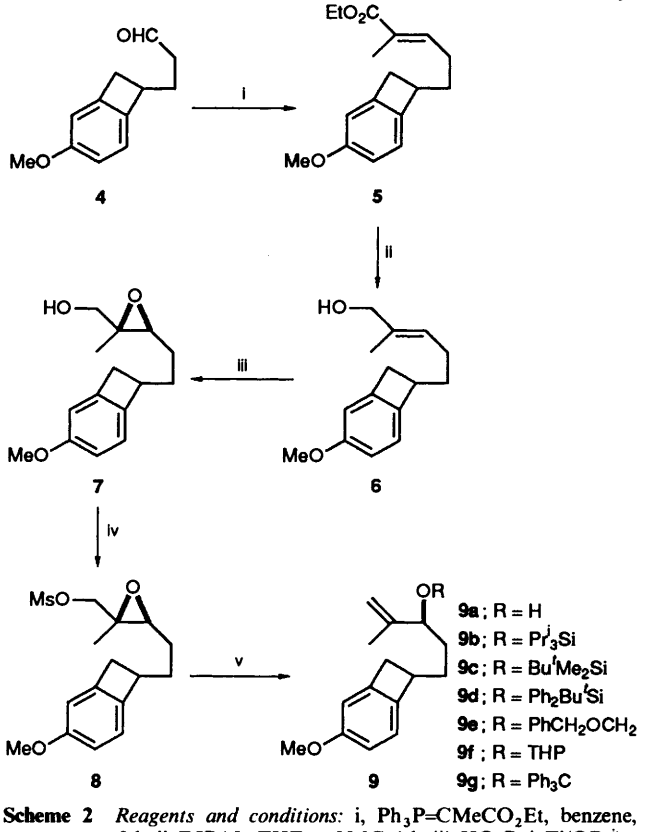
Enantioselectivity in the thermolysis of the optically active alkenic benzocyclobutenes **9a–g** has been studied, resulting in the development of a novel and efficient route to chiral *trans*-3a,4,5,9b-tetrahydro-1*H*-benz[*e*]indenes **10** and **11**.

During the course of our studies[2] directed toward the total synthesis of steroids *via trans*-benzoperhydroindan,† des-A B-trienic steroid, our research interest has centred on the asymmetric synthesis[3] of the corresponding 17-keto analogue **1** (steroid numbering) because of its growing importance as a potential synthon for physiologically important steroids.[4] Herein, we wish to report a novel approach to chiral *trans*-benzoperhydroindan which relied on the stereoselective [4 + 2] cycloaddition of olefinic *o*-quinodimethane **3** to give *C, D trans*-fused des-*A B*-trienic steroid **2**.



Scheme 1

The synthesis of the optically active epoxy alcohol **7**, a common intermediate for the synthesis of optically active olefinic benzocyclobutenes **9a–g**, was straightforward, as follows (Scheme 2). The benzocyclobutenyl aldehyde **4**,[5] easily obtainable in large quantities from 4-methoxybenzocyclobutene-1-carbonitrile,[6] was subjected to Wittig reaction ($Ph_3P{=}CMeCO_2Et$) to give selectively the unsaturated ester **5** (96%), which on reduction with diisobutylaluminium hydride (DIBAL) afforded the alcohol **6** (85%). Asymmetric epoxidation of the allyl alcohol **6** was effected by following the Sharpless procedure[7] to give the chiral epoxy alcohol **7** (96%) in high enantiomeric excess (88% e.e.).‡ Mesylation [methanesulphonyl chloride (MsCl), Et_3N] of **7**, followed by reductive epoxide ring opening (Zn, NaI) of **8** afforded the isopropenyl alcohol **9a** (100% overall yield from **7**). Following the standard derivatisation procedure for **9a** furnished the substrates **9b–g** for generating **3** {**9b** [triisopropylsilyl trifluoromethanesulphonate (TIPSOTf), 2,6-lutidine, CH_2Cl_2, 0 °C, 30 min]; **9c** [*tert*-butyldimethylsilyl trifluoromethanesulphonate (TBSOTf), 2,6-lutidine, CH_2Cl_2, 0 °C, 2 h]; **9d** [*tert*-butyldiphenylsilyl chloride (TBDPSCl), imidazole, DMAP, DMF, room temp., 2 d]; **9e** [benzyloxymethyl chloride (BOMCl), Pr^i_2NEt, DMAP, CH_2Cl_2, room temp., 18 h]; **9f** [dihydropyran (DHP), *p*-TsOH, CH_2Cl_2, room temp., 1 h]; **9g** [triphenylmethyl trifluoromethanesulphonate (TrOTf),[8] 2,6-lutidine, CH_2Cl_2, 0 °C, 30 min]}.



Scheme 2 *Reagents and conditions:* i, $Ph_3P{=}CMeCO_2Et$, benzene, room temp., 2 h; ii, DIBAL, THF, −33 °C, 1 h; iii, HO_2Bu^t, $Ti(OPr^i)_4$, (+)-L-diisopropyl tartrate, 4 Å molecular sieves, CH_2Cl_2, −20 °C; 3 h; iv, $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C, 1 h; v, Zn, NaI, DMF, 100 °C, 30 min

Thermolyses of these substrates **9b–g** afforded the *trans*-fused des-*A B*-trienic steroids **10** and **11** selectively in high yields

† For convenience, *trans*-benzoperhydroindan has been used to refer to the *trans*-3a,4,5,9b-tetrahydro-1*H*-benz[*e*]indene structure throughout the discussion section.

‡ The enantiomeric excess of this epoxide **7** was determined by comparing the corresponding α-methoxy-α-trifluoromethylphenylacetate (MTPA ester) **7a** with that ii of the racemic epoxy alcohol i derived by the epoxidation [Bu^tO_2H, $VO(acac)_2$] of the allyl alcohol **6**.

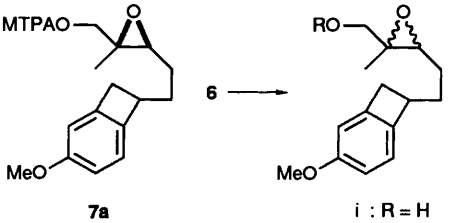
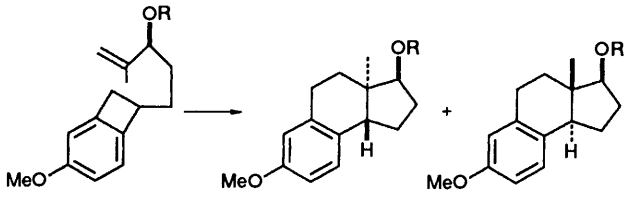


Table 1[a]



Entry	Substrate	Product ratio[b] 10 : 11	Isolated yield[c] (%)
1	**9b**	2:1	81
2	**9c**	2.3:1	100
3	**9d**	1.5:1	94
4	**9e**	1:1.3	89
5	**9f**	1.2:1	72
6	**9g**	1:1	90

[a] All reactions were run under argon in boiling *o*-dichlorobenzene for 3 h. [b] The ratio of isomers **10** and **11** was determined by ^{1}H NMR integration of angular methyl signals [0.56 ppm for **10** (R = H) and 0.63 ppm for **11** (R = H)] of the corresponding alcohols which were derived as follows. For entries 1–3, initial products were desilylated [Bu_4NF, THF, room temp., 2 h] and for entries 4 and 5, initial products were treated with 10% HCl. For entry 6, initial product was treated with TsOH in MeOH. [c] All yields were based on purified products by passing through a short column (SiO_2).

(Table 1). The isomers **11** and **10** were easily separated on silica gel column chromatography and were oxidized [pyridinium chlorochromate (PCC), CH_2Cl_2, 2 h, room temp.] to give the ketone **1**[9] (57%) and its enantiomer (74%) respectively. Thus, we could show that either chiral *trans*-benzoperhydroindan **1** or its enantiomer could be synthesised by using either chiral catalyst in the asymmetric epoxidation step.

Experimental

General Methods.—M.p.s were determined on a Yanagimoto MP-22 apparatus and are uncorrected. IR spectra were recorded on a JASCO IR Report-100. NMR spectra were obtained on JEOL FX-90 and JNM GX-500 spectrometers. Chemical shifts were recorded relative to internal $SiMe_4$. *J* Values are given in Hz. Mass spectra were taken on a JEOL-TMS-O1SG-2, JEOL-AX-500 and JEOL-JMS-DX-303 spectrometers. Optical rotations were measured with a JASCO-DIP-340 polarimeter. $[\alpha]_D$ Values are given in 10^{-1} deg cm^2 g^{-1}. All reactions were carried out under dry nitrogen or dry argon. Column chromatography was carried out with silica gel (Waki gel C-200). The phrase 'residue upon work-up' refers to the residue obtained when the organic layer was separated, dried over anhydrous Na_2SO_4, and the solvent was evaporated off under reduced pressure. All new compounds described in the Experimental section were homogeneous on TLC.

Ethyl 5-(4-Methoxybenzocyclobuten-1-yl)-2-methylpent-2-enoate **5**.—To a stirred solution of the aldehyde **4** (320 mg, 1.7 mmol) in benzene (20 cm^3) at room temperature was added (ethoxycarbonylethylidene)triphenylphosphorane (793 mg, 2.2 mmol). After being stirred for 2 h at the same temperature, the reaction mixture was treated with saturated aq. NaCl and extracted with CH_2Cl_2. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1 v/v) to give the *ester* **5** (443 mg, 96%) as an oil (Found: C, 74.6; H, 7.95%; M$^+$, 274.1613. $C_{15}H_{18}O_2$ requires C, 74.45; H, 8.1%; *M*, 274.1568); $\nu_{max}(CHCl_3)$/cm^{-1} 1710 (C=O); δ_H(90 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.3, OCH_2CH_3), 1.85 (3 H, s, $C{=}CCH_3$), 3.78 (3 H, s, OCH_3), 4.18 (2 H, q, *J* 7.3, OCH_2CH_3) and 6.65–7.05 (3 H, m, ArH); *m/z* 274 (M$^+$).

5-(4-Methoxybenzocyclobuten-1-yl)-2-methylpent-2-en-1-ol **6**.—To a stirred solution of the ester **5** (820 mg, 3.0 mmol) in THF (30 cm^3) at −33 °C was added DIBAL (1.0 mol dm^{-3} hexane solution; 9.0 cm^3, 9.0 mmol) and the reaction mixture was stirred for 1 h at −33 °C, and treated with saturated aq. NH_4Cl, and then filtered through Celite. The separated aqueous layer was extracted with ether and the combined organic layer was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (4:1 v/v) to give the *alcohol* **6** (590 mg, 85%) as an oil (Found: M$^+$, 232.1463. $C_{15}H_{20}O_2$ requires *M*, 232.1462); $\nu_{max}(CHCl_3)$/cm^{-1} 3400 (OH); δ_H(500 MHz; $CDCl_3$) 1.69 (3 H, s, $C{=}CCH_3$), 3.77 (3 H, s, OCH_3), 4.01 (2 H, s, CH_2OH), 5.47 (1 H, t, *J* 7.5, HC=C) and 6.68–6.99 (3 H, m, ArH); *m/z* 232 (M$^+$).

(2S,3S)-2,3-Epoxy-5-(4-methoxybenzocyclobuten-1-yl)-2-methylpentan-1-ol **7**.—To a stirred suspension of 4 Å molecular sieves (150 mg) in CH_2Cl_2 (7 cm^3) at −5 °C were added a solution of (+)-L-diisopropyl tartrate (45 mg, 0.19 mmol) in CH_2Cl_2 (0.2 cm^3), then *tert*-butyl hydroperoxide (3.5 mol dm^{-3} CH_2Cl_2 solution; 1.1 cm^3, 3.85 mmol) at −20 °C, and stirring was continued for 10 min at the same temperature. To this mixture was added dropwise a solution of the allyl alcohol **6** (591 mg, 2.54 mmol) in CH_2Cl_2 (2 cm^3). After being stirred for 3 h at the same temperature, the reaction mixture was treated with water, saturated aq. NaCl, and 10% NaOH, and stirred for 30 min, and then extracted with CH_2Cl_2. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (5:1 v/v) to give the *epoxide* **7** (603 mg, 96%) as an oil (Found: M$^+$, 248.1412. $C_{15}H_{20}O_3$ requires *M*, 248.1411); $\nu_{max}(CHCl_3)$/cm^{-1} 3440 (OH); δ_H(90 MHz; $CDCl_3$) 1.28 (3 H, s, CH_3), 3.75 (3 H, s, OCH_3) and 6.68–7.03 (3 H, m, ArH); *m/z* 248 (M$^+$).

(2S,3S,1'S)-2,3-Epoxy-5-(4-methoxybenzocyclobuten-1-yl)-1-(α-methoxy-α-trifluoromethylphenylacetoxy)-2-methylpentane **7a**.—To a stirred solution of the alcohol **7** (5.6 mg, 0.023 mmol), (*S*)-(−)-α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) (11.7 mg, 0.05 mmol) and dimethylaminopyridine (DMAP) (2.8 mg, 0.023 mmol) in CH_2Cl_2 (2 cm^3) at 0 °C was added a solution of dicyclohexylcarbodiimide (DCC) (9.5 mg, 0.046 mmol) in CH_2Cl_2 (1 cm^3). After being stirred for 12 h at room temperature, the reaction mixture was diluted with ether and washed successively with 10% HCl, saturated aq. $NaHCO_3$ and aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1 v/v) to give the *MTPA ester* **7a** (10.3 mg, 96%) as an oil (Found: M$^+$, 468.1811. $C_{25}H_{27}F_3O_5$ requires *M*, 468.1809); $\nu_{max}(CHCl_3)$/cm^{-1} 1750 (C=O); δ_H(500 MHz; $CDCl_3$) 1.32 (3 H, s, CH_3), 3.57 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 4.16 (0.12 H, d, *J* 12.0, $CH_2OC{=}O$), 4.24 (0.88 g, d, *J* 12.0, $CH_2OC{=}O$), 4.36 (0.88 H, d, *J* 12.0, $CH_2OC{=}O$), 4.40 (0.12 H, d, *J* 12.0, $CH_2OC{=}O$), 6.70–7.00 (3 H, m, ArH) and 7.40–7.58 (5 H, m, ArH); *m/z* 568 (M$^+$).

(1'S)-2,3-Epoxy-5-(4-methoxybenzocyclobuten-1-yl)-1-(α-methoxy-α-trifluoromethylphenylacetoxy)-2-methylpentane **7a** ii. —To a stirred solution of the allyl alcohol **6** (27.3 mg, 0.118 mmol) and a catalytic amount of vanadium acetylacetonate in CH_2Cl_2 (2 cm^3) at 0 °C was added *tert*-butyl hydroperoxide (3.5 mol dm^{-3} CH_2Cl_2 solution: 0.1 cm^3, 0.35 mmol). After being stirred for 30 min at the same temperature, the reaction mixture was passed through silica gel. The mixture of the residue resulting from evaporation of the solvent, (*S*)-(−)-MTPA (55.3 mg, 0.24 mmol) and DMAP (14.4 mg, 0.118 mmol) were

dissolved in CH_2Cl_2 (2 cm^3) and treated with DCC (51.6 mg, 0.25 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature, diluted with ether and washed successively with 10% HCl, saturated aq. $NaHCO_3$, and aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1 v/v) to give the *MTPA ester* **ii** (49.3 mg, 90%) as an oil (Found: M^+, 468.1810); $\nu_{max}(CHCl_3)/cm^{-1}$ 1750; δ_H(500 MHz; $CDCl_3$) 1.32 (3 H, s, CH_3), 3.57 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 4.16 (0.5 H, d, *J* 12.0, CH_2OC=O), 4.24 (0.5 H, d, *J* 12.0, CH_2OC=O), 4.36 (0.5 H, d, *J* 12.0, CH_2OC=O), 4.40 (0.5 H, d, *J* 12.0, CH_2OC=O), 6.70–7.00 (3 H, m, ArH) and 7.40–7.58 (5 H, m, ArH); *m/z* 468 (M^+).

(3S)-5-(4-*Methoxybenzocyclobuten*-1-*yl*)-2-*methylpent*-1-*en*-3-*ol* **9a**.—To a stirred solution of the alcohol **7** (203 mg, 0.83 mmol) and Et_3N (0.31 cm^3, 2.06 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C was added methanesulphonyl chloride (MsCl) (0.13 cm^3, 1.65 mmol). After being stirred for 1 h at the same temperature, the reaction mixture was washed successively with 10% HCl and saturated aq. $NaHCO_3$. The residue upon work-up, NaI (247 mg, 1.65 mmol) and Zn (150 mg) were suspended in *N,N*-dimethylformamide (DMF) (10 cm^3). After the reaction mixture has been stirred for 30 min at 100 °C, it was treated with water and filtered through Celite. The filtrate was extracted with ether and the extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (4:1 v/v) to give the *allyl alcohol* **9a** (192 mg, 100%) as an oil (Found: C, 77.3; H, 8.65%; M^+, 232.1963. $C_{15}H_{20}O_2$ requires C, 77.55; H, 8.7%; *M*, 232.1462); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 (OH); δ_H(90 MHz; $CDCl_3$) 1.75 (3 H, s, CH_3), 3.75 (3 H, s, OCH_3), 4.83, 4.95 (each 1 H, each s, C=CH_2) and 6.63–7.08 (3 H, m, ArH); *m/z* 232 (M^+).

(3S,3aR,9bS)-trans-2,3,3a,4,5,9b-*Hexahydro*-7-*methoxy*-3aα-*methyl*-1H-*benz*[e]*inden*-3β-*ol*, **10** *and* (3S,3aR,9bR)-trans-2,3,3a,4,5,9b-*Hexahydro*-7-*methoxy*-3aβ-*methyl*-1H-*benz*[e]-*inden*-3β-*ol* **11**.—(*a*) Via *thermolysis of* (3S)-5-(4-*methoxybenzocyclobuten*-1-*yl*)-2-*methyl*-3-*triisopropylsiloxypent*-1-*ene* **9b**. To a stirred solution of the alcohol **9a** (190 mg, 0.82 mmol) and 2,6-lutidine (0.36 cm^3, 3.11 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C was added dropwise TIPSOTf (0.40 cm^3, 1.47 mmol). After being stirred for 30 min at the same temperature, the reaction mixture was treated with saturated aq. NaCl and extracted with CH_2Cl_2. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1 v/v) to give the silyl ether **9b** as an oil. The solution of the silyl ether **9b** obtained above in *o*-dichlorobenzene (20 cm^3) was refluxed for 3 h under a current of argon. The residue resulting from evaporation of the solvent was dissolved in THF (5 cm^3) and treated with Bu_4NF (1.0 mol dm^{-3} THF solution: 3.2 cm^3, 3.2 mmol). After being stirred for 2 h at room temperature, the reaction mixture was diluted with water and extracted with ether. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (98:2 v/v) to give the *alcohol* **10** (101 mg, 54%) as needles, m.p. 94–95 °C (from ether); $[\alpha]_D^{20}$ +6.35 (*c* 1.70 in $CHCl_3$) (Found: M^+, 232.1463. $C_{15}H_{20}O_2$ requires *M*, 232.1462); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 (OH); δ_H(90 MHz; $CDCl_3$) 0.56 (3 H, s, CH_3), 3.73 (3 H, s, OCH_3) and 6.60–7.05 (3 H, m, ArH); *m/z* 232 (M^+). Further elution with hexane–ethyl acetate (95:5 v/v) afforded the *alcohol* **11** (52 mg, 27%) as an oil, $[\alpha]_D^{20}$ +18.19 (*c* 1.77 in $CHCl_3$) (Found: M^+, 232.1463); $\nu_{max}(CHCl_3)/cm^{-1}$ 3410 (OH); δ_H(90 MHz; $CDCl_3$) 0.63 (3 H, s, CH_3), 3.75 (3 H, s, OCH_3) and 6.55–6.95 (3 H, m, ArH); *m/z* 232 (M^+).

(*b*) Via *thermolysis of* (3S)-3-tert-*butyldimethylsiloxy*-5-(4-*methoxybenzocyclobuten*-1-*yl*)-2-*methylpent*-1-*ene* **9c**. By following exactly the same procedure as described for **9b** using TBSOTf (0.044 cm^3, 0.19 mmol) in place of TIPSOTf, the alcohol **9** (25 mg, 0.11 mmol) afforded a mixture of **10** and **11** (25 mg, 100%) in a ratio of 2.3:1.

(*c*) Via *thermolysis of* (3S)-3-tert-*butyldiphenylsiloxy*-5-(4-*methoxybenzocyclobuten*-1-*yl*)-2-*methylpent*-1-*ene* **9d**. To a stirred solution of the alcohol **9d** (65 mg, 0.28 mmol), a catalytic amount of DMAP and imidazole (48 mg, 0.7 mmol) in DMF (5 cm^3) at room temperature was added dropwise TBDPSCl (0.15 cm^3, 0.56 mmol). After being stirred for 2 d at room temperature, the reaction mixture was treated with saturated aq. NaCl and extracted with ether. The residue upon work-up was chromatographed and then subjected successively to the thermolysis and deprotection by following exactly the same procedure described for **9b** to give a mixture of **10** and **11** (61 mg, 94%) in a ratio of 1.5:1.

(*d*) Via *thermolysis of* (3S)-3-*benzyloxymethoxy*-5-(4-*methoxybenzocyclobuten*-1-*yl*)-2-*methylpent*-1-*ene* **9e**. To a stirred solution of the alcohol **9a** (25 mg, 0.11 mmol), a catalytic amount of DMAP and Pr^i_2NEt (0.16 cm^3, 0.88 mmol) in CH_2Cl_2 (2 cm^3) at 0 °C was added dropwise BOMCl (0.092 cm^3, 0.66 mmol) and the mixture was stirred for 18 h at room temperature, treated with water and extracted with CH_2Cl_2. The extract was washed with 10% HCl and saturated aq. $NaHCO_3$. The residue upon work-up was chromatographed with hexane–ethyl acetate (4:1 v/v) to give the BOM ether **9e** as an oil. After thermolysis of **9e** using the same procedure as described for **9b**, the crude product was dissolved in MeOH (10 cm^3) and 10% HCl (1 cm^3). After being refluxed for 30 min, the reaction mixture was basified with saturated aq. $NaHCO_3$ and evaporated to leave the residue which was extracted with ether. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed by following the same procedure for **9b** to give a mixture of **10** and **11** (21 mg, 89%) in a ratio of 1:1.3.

(*e*) Via *thermolysis of* (3S)-5-(4-*methoxybenzocyclobuten*-1-*yl*)-3-(*tetrahydropyranyloxy*)-2-*methylpent*-1-*ene* **9f**. A mixture of the alcohol **9a** (14 mg, 0.059 mmol), a catalytic amount of *p*-TsOH, DHP (0.11 cm^3, 0.12 mmol) and CH_2Cl_2 (10 cm^3) was stirred for 1 h at room temperature and then washed with saturated aq. $NaHCO_3$. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1 v/v) to give the THP ether **9f**. By following the same procedure as described for **9e**, thermolysis, deprotection and purification of **9f** gave the mixture of **10** and **11** (9.9 mg, 72%) in a ratio of 1.2:1.

(*e*) Via *thermolysis of* (3S)-5-(4-*methoxybenzocyclobuten*-1-*yl*)-3-*triphenylmethoxy*-2-*methylpent*-1-*ene* **9g**. To a stirred suspension of silver trifluoromethanesulphonate (543 mg, 2.11 mmol) was added triphenylmethyl chloride (584 mg, 2.09 mmol) at 0 °C and the mixture was stirred for 30 min at the same temperature. To this reaction mixture was added a solution of the alcohol **9a** (205 mg, 0.882 mmol) in CH_2Cl_2 (6 cm^3) and 2,6-lutidine (0.5 cm^3, 4.29 mmol) at 0 °C. After stirring had been continued for 30 min at the same temperature, the reaction mixture was filtered through Celite and was washed with saturated aq. $NaHCO_3$ and aq. NaCl successively. The residue upon work-up was chromatographed with hexane–ethyl acetate (97:3 v/v) to give the trityl ether **9g**. After thermolysis of **9g**, the crude product was dissolved in MeOH (5 cm^3) containing a catalytic amount of *p*-TsOH. After being refluxed for 11 h, the reaction mixture was evaporated to leave the residue which was chromatographed to give the mixture of **10** and **11** (184 mg, 90%) in a ratio of 1:1.

(3aS,9bR)-7-*Methoxy*-3aβ-*methyl*-3a,4,5,9b-*tetrahydro*-1H-*inden*-3(2H)-*one* **1**.—To a stirred solution of the alcohol **11** (17 mg, 0.07 mmol) in CH_2Cl_2 (5 cm^3) at room temperature was added portionwise PCC (79 mg, 0.37 mmol). After being stirred for 2 h at the same temperature, the mixture was treated with 10% NaOH and extracted with CH_2Cl_2. The extract was

washed with 10% HCl and saturated aq. $NaHCO_3$. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1 v/v) to give the ketone **1** (9.6 mg, 57%) as plates, m.p. 90–91 °C (from EtOH) (lit.,[7] 89 °C); $[\alpha]_D^{20}$ +107 (*c* 0.4 in MeOH) (lit.,[7] +99) (Found: M^+, 230.1307. $C_{15}H_{18}O_2$ requires *M*, 230.1306); $\nu_{max}(CHCl_3)/cm^{-1}$ 1740 (C=O); δ_H(90 MHz; $CDCl_3$) 0.74 (3 H, s, CH_3), 3.80 (3 H, s, OCH_3) and 6.60–7.10 (3 H, m, ArH); *m/z* 230 (M^+).

(3aS,9bR)-7-*Methoxy*-3aα-*methyl*-3a,4,5,9b-*tetrahydro*-1H-*inden*-3(2H)-*one* (*enantiomer of* **1**). By following exactly the same procedure as described for **1**, the alcohol **10** (33 mg, 0.14 mmol) afforded the ketone (enantiomer of **1**) (24 mg, 74%) as plates, m.p. 103–104 °C (from EtOH); $[\alpha]_D^{20}$ −109 (*c* 0.73 in MeOH). This was identical with **1** (IR, NMR and mass spectra).

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