Asymmetric Construction of α,α-Disubstituted Cyclobutanones—Enantioselective Total Synthesis of (−)-Frontalin

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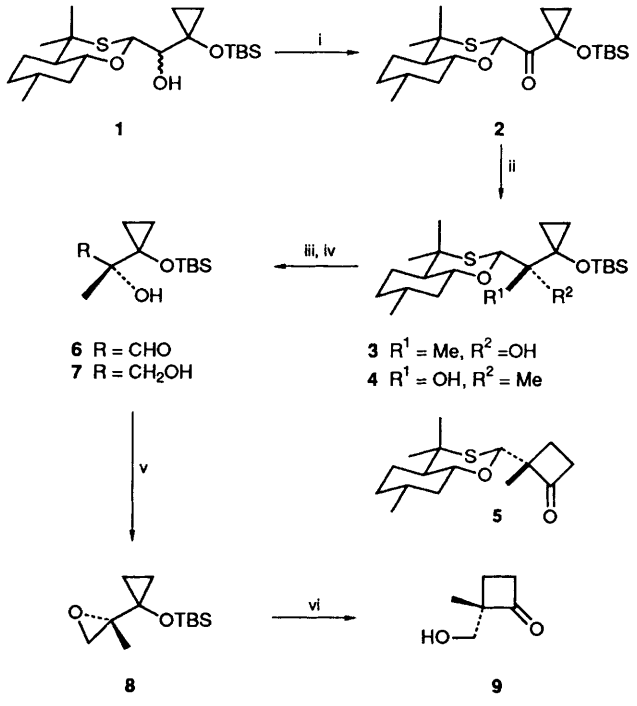
Novel access to the chiral, α,α-disubstituted ketone 2-hydroxymethyl-2-methylcyclobutanone was developed, leading to an enantioselective total synthesis of (−)-frontalin, an aggregating pheromone of bark beetles.

The construction of chiral quaternary stereogenic centres[1] is one of the most important problems in the enantioselective synthesis[2] of natural products. We report herein a potentially valuable method for the enantioselective construction of quaternary carbons *via* enantiospecific 1,2-rearrangements of cyclopropane systems to produce chiral α,α-disubstituted cyclobutanones, which lead to an enantioselective total synthesis of (−)-frontalin **18**.

Our preliminary goal in this context relied on an enantioselective construction of the chiral cyclopropyl epoxide **8**, followed by its enantiospecific 1,2-rearrangement. Hence, the ketone **2**, prepared in 79% yield by Swern oxidation of a diastereoisomeric mixture of the optically active alcohol **1**,[3] was subjected to Grignard reaction (MeMgBr) to give the alcohol **3** (91%) as a single product with no detectable amount of the isomeric alcohol **4**. This high stereoselectivity could be reasonably explained by applying a cyclic Cram's model, with the magnesium chelating with the ring oxygen and the carbonyl group, followed by attack from the least hindered side of the carbonyl group as mentioned in Eliel's original report.[4] (The direct 1,2-rearrangement of the alcohol **3** to produce the corresponding cyclobutanone **5** was first examined, and the reaction was found not to be like the case for the secondary alcohol[3]). Oxidative solvolysis [*N*-chlorosuccinimide (NCS), $AgNO_3$] of the alcohol **3** afforded the aldehyde **6**, which was reduced ($NaBH_4$) to give the diol **7** (92% overall yield from **3**). Mesylation [methanesulphonyl chloride (MsCl), Et_3N] of the diol **7**, followed by base (NaH) treatment of the resulting monomesyl ester, yielded the epoxide **8**, which on treatment with silica gel furnished the cyclobutanone **9** (99% overall yield from **7**) (Scheme 1).



Scheme 1 *Reagents and conditions*: i, $(COCl)_2$, DMSO, CH_2Cl_2, −78 °C; then Et_3N, 0 °C; ii, MeMgBr, THF, −78 °C; iii, NCS, $AgNO_3$, aq. MeCN–CH_2Cl_2, 0 °C; iv, $NaBH_4$, EtOH, 0 °C; v, MsCl, Et_3N, CH_2Cl_2; then NaH, EtOH; vi, SiO_2, CH_2Cl_2, room temp.

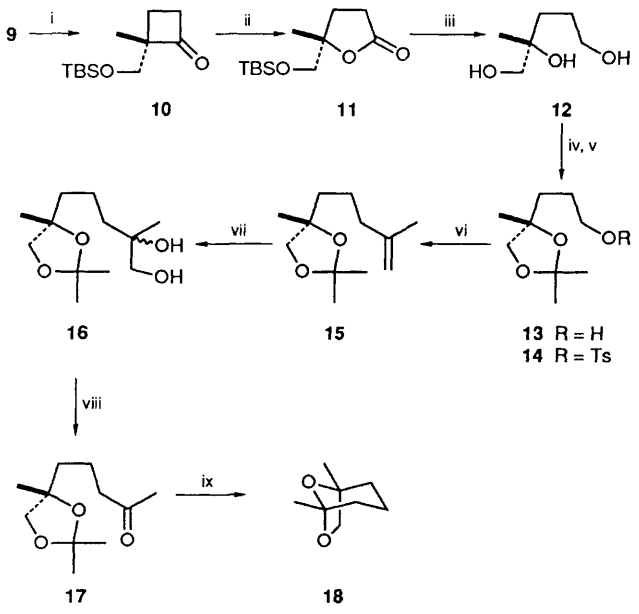
Confirmation of the absolute configuration and also the enantiomeric purity of this cyclobutanone **9** was achieved by a demonstration of the effective synthesis of (−)-frontalin **18** starting from ketone **9** as follows.

Protection [*t*-butylchlorodimethylsilane (TBSCl), Et_3N] of the alcohol **9** afforded the silyl ether **10** (74%), which was then subjected to Baeyer–Villiger oxidation [*m*-chloroperbenzoic acid (MCPBA)] to give the lactone **11** (85%). The triol **12**, obtained by reduction [lithium aluminium hydride (LAH)] of the lactone **11**, was protected [2,2-dimethoxypropane, toluene-*p*-sulphonic acid (PTSA)] to give the acetonide alcohol **13**[4] (76% overall yield from **11**), which was tosylated [toluene-*p*-sulphonyl chloride (*p*-TsCl), pyridine] to afford the tosyl ester **14** (64%). Coupling of this tosate **14** with isopropenylmagnesium bromide was effected in the presence of dilithium tetrachlorocuprate (Li_2CuCl_4) to produce the olefin **15** (81%). Osmylation [osmium tetraoxide (OsO_4), *N*-methylmorpholine oxide (NMO)] of this olefin **15**, followed by oxidative cleavage [sodium metaperiodate ($NaIO_4$)] of the resulting diol **16**, yielded the keto acetonide **17** (76% overall yield from the olefin **15**). Finally, the keto acetonide **17** was treated with acid (PTSA) to furnish our target molecule, (−)-frontalin **18** (Scheme 2), which was identical with an authentic sample[5,6] in all aspects, including its optical behaviour.

Thus we have developed a novel route to the chiral α,α-disubstituted cyclobutanone **9** and have shown its flexibility by illustrating an effective synthesis of (−)-frontalin **18**.

Experimental

General Methods.—M.p.s were determined on a Yanagimoto MP-22 apparatus and are uncorrected. IR spectra were recorded on a JASCO Report-100 spectrophotometer. ^1H NMR spectra were obtained on a JEOL FX-90 spectrometer. Chemical shifts were recorded relative to internal $SiMe_4$, and *J*-values are in Hz. Mass spectra were taken on a JEOL-JMS-01SG-2, JEOL-AX-500, or JEOL-JMS-DX-303 spectrometer. Optical rorations were measured with a JASCO-DIP-340 polarimeter. All reactions were carried out under dry nitrogen. Column chromatography was carried out with silica gel (Wako gel C-200). The phrase 'residue upon work-up' refers to the residue obtained when the organic layer was separated, dried



Scheme 2 *Reagents and conditions:* i, TBSCl, Et_3N, CH_2Cl_2, room temp.; ii, MCPBA, aq. $NaHCO_3$, CH_2Cl_2, 0 °C; iii, LAH, THF, 0 °C; iv, $Me_2C(OMe)_2$, PTSA, acetone; v, *p*-TsCl, pyridine, 0°C; vi, isopropenylmagnesium bromide, Li_2CuCl_4, THF, −78 °C ⟶ room temp.; vii, OsO_4, NMO, acetone–water, room temp.; viii, $NaIO_4$, acetone, room temp.; ix, PTSA, Et_2O–water, reflux.

over anhydrous Na_2SO_4, and the solvent was evaporated off under reduced pressure. All new compounds described in this Experimental section were homogeneous on TLC.

(2R,4aR,7R,8aR)-[1-(t-*Butyldimethylsiloxy*)*cyclopropyl*]-(4a,5,6,7,8,8a-*hexahydro*-4,4,7-*trimethyl*-4H-1,3-*benzoxathian*-2-*yl*)*methanone* **2**.—To a stirred solution of dimethyl sulphoxide (DMSO) (1.84 cm^3, 26.0 mmol) in CH_2Cl_2 (50 cm^3) at −78 °C was added oxalyl dichloride (1.42 cm^3, 16.2 mmol). After the mixture had been stirred for 10 min at −78 °C a solution of the alcohol **1** (2.6 g, 6.49 mmol) in CH_2Cl_2 (10 cm^3) was added and the mixture was stirred for 30 min at the same temperature before being treated with Et_3N (4.98 cm^3, 35.7 mmol), allowed to warm to 0 °C, quenched with 10% aq. HCl, and extracted with CH_2Cl_2. The extract was washed successively with saturated aq. $NaHCO_3$, water, and saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (97:3) to give the *ketone* **2** (2.03 g, 79%) as an oil, $[\alpha]_D^{26}$ −47.97° (*c* 1.04, $CHCl_3$) (Found: C, 63.25; H, 9.7. $C_{21}H_{38}O_3SSi$ requires C, 63.25; H, 9.6%); ν_{max}(neat)/cm^{-1} 1718 (C=O); δ_H($CDCl_3$) 0.18 (6 H, s, $SiMe_2$), 0.73–1.07 (4 H, m, CH_2CH_2), 0.91 (9 H, s, SiBu^t), 0.94 (3 H, d, *J* 7, 7-Me), 1.30 and 1.49 (6 H, each s, 4-Me_2), 3.43 (1 H, dt, *J* 4 and 10, 8a-H) and 6.03 (1 H, s, 2-H); *m*/*z* 398 (M^+).

(2R,4aR,7R,8aR)-1-[1-(t-*Butyldimethylsiloxy*)*cyclopropyl*]-1-(4a,5,6,7,8,8a-*hexahydro*-4,4,7-*trimethyl*-4H-1,3-*benzoxathian*-2-*yl*) *ethanol* **3**.—To a stirred solution of the ketone **2** (105 mg, 0.26 mmol) in tetrahydrofuran (THF) (5 cm^3) at −78 °C was added a 3.0 mol dm^{-3} ethereal solution of methylmagnesium bromide (0.17 cm^3, 0.51 mmol). After the mixture had been stirred for 30 min at the same temperature it was treated with saturated aq. NH_4Cl and extracted with diethyl ether. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (98:2) to give the *alcohol* **3** (99.2 mg, 91%) as needles, m.p. 96–97 °C (from pentane); $[\alpha]_D^{22}$ −29.24° (*c* 1.06, $CHCl_3$) (Found: C, 63.85; H, 10.3. $C_{22}H_{42}O_3SSi$ requires C, 63.65; H, 10.2%); ν_{max}(KBr)/cm^{-1} 3570 (OH); δ_H($CDCl_3$) 0.07 (6 H, s, $SiMe_2$), 0.55–0.85 (4 H, m, CH_2CH_2), 0.88 (9 H, s, SiBu^t), 0.93 (3 H, d, *J*, 7, 7-Me), 1.28 and 1.42 (6 H, each s, 4-Me_2), 1.35 [3 H, s, CH(OH)*Me*], 3.43 (1 H, dt, *J* 4 and 10, 8a-H) and 5.24 (1 H, s, 2-H); *m*/*z* 414 (M^+).

(R)-1-[1-(t-*Butyldimethylsiloxycyclopropyl*]-1-*methylethane*-1,2-*diol* **7**.—To a stirred mixture of NCS (458 mg, 3.43 mmol) and $AgNO_3$ (675.5 mg, 3.98 mmol) in MeCN (9 cm^3)–water (1 cm^3) at 0 °C was added a solution of the alcohol **3** (474 mg, 1.14 mmol) in CH_2Cl_2 (1 cm^3)–MeCN (1 cm^3). The mixture was then stirred for 15 min at 0 °C and treated successively with saturated aq. Na_2SO_3, saturated aq. Na_2CO_3, and aq. NaCl; it was then filtered through Celite. The filtrate was extracted with CH_2Cl_2 and the extract was washed with saturated aq. Na_2CO_3. The residue upon work-up was chromatographed with hexane–ethyl acetate (97:3) to give the aldehyde **6** as an oil, which was immediately subjected to the next reaction because of its instability.

To a stirred solution of the aldehyde in EtOH (1 cm^3) at 0 °C was added portionwise $NaBH_4$ (64.8 mg, 1.71 mmol) and the mixture was stirred for 10 min at the same temperature before being diluted with water and extracted with CH_2Cl_2. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (8:2) to give the *diol* **7** (258.5 mg, 92% overall yield from **3**) as an oil, $[\alpha]_D^{23}$ −12.81° (*c* 1.03, $CHCl_3$) [Found: (M^+ − 17), 229.1624. $C_{12}H_{25}O_2SSi$ requires *m*/*z*, 229.1640]; ν_{max}(neat)/cm^{-1} 3400 (OH); δ_H($CDCl_3$) 0.07 (6 H, s, $SiMe_2$), 0.53–0.81 (4 H, m, CH_2CH_2), 0.82 (9 H, s, SiBu^t), 1.14 (3 H, s, Me), 1.61 and 2.25 (2 H, each br s, OH) and 3.32–3.89 (2 H, m, CH_2OH); *m*/*z* 229 (M^+ − 17).

(S)-2-*Hydroxymethyl*-2-*methylcyclobutanone* **9**.—To a stirred solution of the diol **7** (160 mg, 0.65 mmol) and Et_3N (0.11 cm^3, 1.50 mmol) in CH_2Cl_2 (1.2 cm^3) at 0 °C was added dropwise MsCl (0.05 cm^3, 0.65 mmol). The mixture was then stirred for 1 h at the same temperature, diluted with aq. 10% HCl, and extracted with CH_2Cl_2. The residue upon work-up was used directly for the next reaction without further purification.

To a stirred solution of the crude monomesate in EtOH (1 cm^3) at 0 °C was added portionwise a 60% suspension of NaH in oil (26.4 mg, 0.65 mmol). After the mixture had been stirred for 30 min at the same temperature it was diluted with diethyl ether and washed with saturated aq. NaCl. The residue upon work-up was chromatographed on silica gel with CH_2Cl_2 to give the *cyclobutanone* **9** (73 mg, 99% overall yield from the diol **7**) as an oil, $[\alpha]_D^{22}$ −18.5° (*c* 0.94, $CHCl_3$) (Found: M^+, 114.0681. $C_6H_{10}O_2$ requires M, 114.0680); ν_{max}(neat)/cm^{-1} 3420 (OH) and 1778 (C=O); δ_H($CDCl_3$; 500 MHz) 1.22 (3 H, s, Me), 1.61 (1 H, br s, OH), 1.75–1.82 (1 H, m, 3-H), 2.16–2.25 (1 H, m, 3-H), 2.95–3.10 (2 H, m, 4-H_2) and 3.58 and 3.73 (2 H, each d, *J* 10.3, CH_2OH); *m*/*z* 114 (M^+).

(S)-2-t-*Butyldimethylsiloxymethyl*-2-*methylcyclobutanone* **10**.—To a stirred solution of the cyclobutanone **9** (73.8 mg, 0.65 mmol) and Et_3N (0.18 cm^3, 1.29 mmol) in CH_2Cl_2 (1.2 cm^3) at 0 °C was added portionwise TBSCl (146 mg, 0.97 mmol). After the reaction mixture had been stirred for 12 h at room temperature it was treated with 10% aq. HCl and extracted with CH_2Cl_2. The extract was washed successively with saturated aq. $NaHCO_3$ and aq. NaCl. The residue upon work-up was chromatographed with hexane to give the *silyl ether* **10** (109 mg, 74%) as an oil, $[\alpha]_D^{22}$ −34.6° (*c* 1.00, $CHCl_3$) [Found: (M^+ − 57), 171.0841. $C_8H_{15}O_2Si$ requires *m*/*z*, 171.0840]; ν_{max}(neat)/cm^{-1} 1780 (C=O); δ_H($CDCl_3$) 0.02 and

0.04 (6 H, each s, $SiMe_2$), 0.86 (9 H, s, $SiBu^t$), 1.10 (3 H, s, Me), 1.49–2.46 (2 H, m, 3-H_2), 2.77–3.03 (2 H, m, 4-H_2) and 3.39 and 3.70 (2 H, each d, *J* 10.3, CH_2OH); *m/z* 171 ($M^+ - 57$).

(S)-5-t-*Butyldimethylsiloxymethyl*-4,5-*dihydro*-5-*methylfuran*-2(3H)-*one* **11**.—To a stirred solution of the silyl ether **10** (152 mg, 0.66 mmol) in a mixture of CH_2Cl_2 (3 cm^3) and saturated aq. $NaHCO_3$ (3 cm^3) at 0 °C was added portionwise MCPBA (286 mg, 1.33 mmol) and the mixture was stirred for 2 h at the same temperature before being extracted with CH_2Cl_2. The extract was washed successively with 10% aq. NaOH and saturated aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1) to give the *lactone* **11** (138 mg, 85%) as an oil, $[\alpha]_D^{21}$ −1.34° (*c* 1.94, $CHCl_3$) [Found: ($M^+ - 57$), 187.0802. $C_8H_{15}O_3Si$ requires *m/z* 187.0790]; ν_{max}(neat)/cm^{-1} 1780 (C=O); δ_H($CDCl_3$) 0.06 (6 H, s, $SiMe_2$), 0.87 (9 H, s, Bu^t), 1.34 (3 H, s, Me), 1.49–2.89 (4 H, m, CH_2CH_2) and 3.49 and 3.68 (2 H, each d, *J* 9, CH_2OH); *m/z* 187 ($M^+ - 57$).

(S)-3-(2,2,4-*Trimethyl*-1,3-*dioxolan*-4-*yl*)*propan*-1-*ol* **13**.—To a stirred solution of the lactone **11** (264 mg, 1.08 mmol) in THF (2 cm^3) at 0 °C was added a 1 mol dm^{-3} suspension of LAH in THF (1.2 cm^3, 1.20 mmol). After being stirred for 30 min at the same temperature, the reaction mixture was treated with water (0.1 cm^3) and filtered through Celite. The filtrate was evaporated to leave the crude triol **12**, which was used for the next reaction without further purification.

To a stirred solution of the crude triol **12** and 2,2-dimethoxypropane (0.15 cm^3) at room temperature was added a catalytic amount of (PTSA) (10 mg) and the mixture was stirred for 1 h at the same temperature. The reaction mixture was then basified with saturated aq. $NaHCO_3$ and evaporated to leave a residue, which was extracted with ethyl acetate. The extract was washed successively with saturated aq. $NaHCO_3$ and aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1) to give the *acetonide* **13**[4] (142.2 mg, 76% overall yield from **11**) as an oil, $[\alpha]_D^{21}$ −0.80° (*c* 2.47, acetone) [Found: ($M^+ - 15$), 159.1021. $C_8H_{15}O_3$ requires *m/z*, 159.1020]; ν_{max}(neat)/cm^{-1} 3420 (OH); δ_H($CDCl_3$) 1.28 (3 H, s, Me), 1.43 (6 H, s, CMe_2), 1.52–1.83 (4 H, m, CH_2CH_2), 2.19 (1 H, br s, OH), 3.54–3.85 (2 H, m, CH_2OH) and 3.78 (2 H, s, CCH_2O); *m/z* 159 ($M^+ - 15$).

(S)-3-(2,2,4-*Trimethyl*-1,3-*dioxolan*-4-*yl*)*propyl Toluene*-p-*sulphonate* **14**.—To a stirred solution of the acetonide **13** (415 mg, 2.38 mmol) in pyridine (5 cm^3) at 0 °C was added portionwise TsCl (1.36 g, 7.13 mmol). The mixture was stirred for 2 h at room temperature and then diluted with ethyl acetate and washed successively with 10% aq. HCl, saturated aq. $NaHCO_3$, and aq. NaCl. The residue upon work-up was chromatographed with hexane–ethyl acetate (9:1) to give the *tosate* **14** (500 mg, 64%) as an oil, $[\alpha]_D^{21}$ −1.15° (*c* 1.86, $CHCl_3$) [Found: ($M^+ - 15$), 313.1094. $C_{15}H_{21}O_5$ requires *m/z*, 313.1108]; δ_H($CDCl_3$) 1.22 (3 H, s, Me), 1.31 and 1.38 (6 H, each s, m, Me_2), 1.28–2.12 (4 H, m, CH_2CH_2), 2.46 (3 H, s, Ar*Me*), 3.70 (2 H, s, CCH_2O), 4.08 (2 H, t, *J* 7, CH_2OTs), 7.37 (2 H, d, *J* 9, ArH) and 7.79 (2 H, d, *J* 9, ArH); *m/z* 313 ($M^+ - 15$).

(S)-2,2,4-*Trimethyl*-4-(4′-*methylpent*-4′-*enyl*)-1,3-*dioxolane* **15**.—To a stirred solution of the tosate **14** (56.5 mg, 0.17 mmol) in THF (2 cm^3) at −78 °C were added a solution of isopropenylmagnesium bromide in THF (1 mol dm^{-3}; 3 cm^3, 3 mmol) followed by a solution of dilithium tetrachlorocuprate in THF (0.1 mol dm^{-3}; 0.17 cm^3, 0.017 mmol). After being stirred for 15 h at room temperature the reaction mixture was treated with saturated aq. NH_4Cl and extracted with diethyl ether. The extract was washed with saturated aq. NaCl. The residue upon work-up was chromatographed with pentane–diethyl ether (98:2) to give the *olefin* **15** (27.7 mg, 81%) as an oil, $[\alpha]_D^{21}$ −3.60° (*c* 1.35, $CHCl_3$) [Found: ($M^+ - 15$), 183.1379. $C_{11}H_{19}O_2$ requires *m/z*, 183.1384]; ν_{max}(neat)/cm^{-1} 1627 (C=C); δ_H($CDCl_3$) 1.31 (3 H, s, 4-Me), 1.41 (6 H, s, CMe_2), 1.45–1.62 (4 H, m, CH_2CH_2), 1.73 (3 H, s, 4′-Me), 1.86–2.17 (2 H, m, 3′-H_2), 3.68 and 3.80 (2 H, each d, *J* 9, 5-H_2) and 4.70 (2 H, br s, $C{=}CH_2$); *m/z* 183 ($M^+ - 15$).

(S)-5-(2,2,4-*Trimethyl*-1,3-*dioxolan*-4-*yl*)*pentan*-2-*one* **17**.—To a stirred solution of the olefin **15** (27.7 mg, 0.14 mmol) in water–acetone (5:2, 7 cm^3) at room temperature was added NMO (18.0 g, 0.15 mmol) followed by a catalytic amount of OsO_4. After being stirred for 30 min at the same temperature, the reaction mixture was treated with $NaIO_4$ (59.8 mg, 0.28 mmol) and stirred for a further 30 min at the same temperature; it was then evaporated to leave a residue, which was extracted with diethyl ether. The extract was washed successively with 10% aq. HCl, saturated aq. $NaHCO_3$, and aq. NaCl. The residue upon work-up was chromatographed with pentane–diethyl ether (7:3) to give the *ketone* **17** (21.3 mg, 76% overall yield from **15**) as an oil, $[\alpha]_D^{20}$ −9.45° (*c* 1.06, MeOH) [Found: ($M^+ - 15$), 159.1021. $C_8H_{15}O_3$ requires *m/z*, 159.1020]; ν_{max}(neat)/cm^{-1} 1719 (C=O); δ_H($CDCl_3$) 1.24 (3 H, s, Me), 1.35 (6 H, s, CMe_2), 1.44–1.72 (4 H, m, CH_2CH_2), 2.10 (3 H, s, O=CMe), 2.24–2.61 (2 H, m, $CH_2C{=}O$) and 3.68 and 3.81 (2 H, each d, *J* 9, CH_2OH); *m/z* 159 ($M^+ - 15$).

(S)-(−)-*Frontalin* **18**.—A stirred mixture of the ketone **17** (31.7 mg, 0.16 mmol), a catalytic amount of PTSA (0.5 mg), water (0.1 cm^3) and diethyl ether (3.0 cm^3) was refluxed for 2 h. After the mixture had been basified with powdered K_2CO_3, it was evaporated to leave a residue, which was chromatographed with pentane–diethyl ether (9:1) to give (*S*)-(−)-frontalin **18** (6.7 mg, 30%) as an oil, which was identical with an authentic sample in all aspects, including ^1H NMR, IR and optical rotation data: $[\alpha]_D^{19}$ −53.73° (*c* 0.67, Et_2O) (lit.,[5] −52.0°; lit.,[6] −56.7°).

References

1 S. F. Martin, *Tetrahedron*, 1980, **36**, 419.
2 For leading references on asymmetric synthesis, see T. D. Inch, *Synthesis*, 1970, 466; J. W. Scott and D. Valentine, Jr, *Science*, 1974, **184**, 943; D. Valentine, Jr and J. W. Scott, *Synthesis*, 1978, 329; K. Drauz, A. Kleeman and J. Martens, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 584; K. Hiroi, H. Nakamura and T. Anzai, *J. Am. Chem. Soc.*, 1987, **109**, 1249; I. Ojima, T. Komata and X. Qiu, *J. Am. Chem. Soc.*, 1990, **112**, 770; R. M. Williams, T. Glinka, E. Kwast, H. Coffman and J. K. Stille, *J. Am. Chem. Soc.*, 1990, **112**, 808; E. Lee, I.-J. Shin and T.-S. Kim, *J. Am. Chem. Soc.*, 1990, **112**, 260; M. Isaka and E. Nakamura, *J. Am. Chem. Soc.*, 1990, **112**, 7428.
3 H. Nemoto, H. Ishibashi, M. Mori, S. Fujita and K. Fukumoto, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2835.
4 J. E. Lynch and E. L. Eliel, *J. Am. Chem. Soc.*, 1984, **106**, 2943.
5 K. Mori, *Tetrahedron*, 1975, **31**, 1381.
6 K. Matsuo and Y. Hasuike, *J. Pharm. Soc. Jpn.*, 1990, **110**, 555.

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