The methanol was removed in vacuo and the residue was taken up in ether. The ether solution was washed with water, 50% aqueous ammonium hydroxide, and brine and then dried and concentrated. Distillation at reduced pressure gave 22.3 g (72%) of diester **3** as a clear liquid: bp 84–86 °C (1.0 mm); 100-MHz $^1$H NMR (CDCl$_3$, δ) 1.31 (s, 6 H), 2.52 (s, 2 H), 3.62 (s, 3 H), 3.65 (s, 3 H).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.44; H, 7.06.

**Typical Procedure for Conjugate Addition–Cyclizations. Method A. 2-Carbomethoxy-5,5-dimethyl-3-(2-methyl-2-hepten-6-yl)cyclopent-2-en-1-one (14).** A solution of Grignard reagent [prepared from 2-chloro-6-methyl-5-heptene (10.0 g, 68.7 mmol) and magnesium (3.0 g, 125 mmol)] in 50 mL of dry tetrahydrofuran was added dropwise to a stirred mixture of dry copper(I) iodide (11.05 g, 68.7 mmol) and dry tetramethylenediamine (14.1 mL, 103.1 mmol) in 150 mL of dry THF at −78 °C. This mixture was stirred for 1 h at −78 °C, and a solution of diester **3** (6.0 g, 30.3 mmol) in 10 mL of dry THF was added dropwise. The mixture was stirred at −78 °C for 3 h and warmed to room temperature over 2 h. The reaction was quenched by slowly pouring the mixture into 10% HCl. The mixture was extracted with ether, and the ether layer was washed with saturated sodium bicarbonate, dried, and concentrated. Flash chromatography of the residue on 200 g of silica with 5% ethyl acetate/hexane gave 3.903 g (46%) of **14** as a pale yellow oil: 250-MHz $^1$H NMR (CDCl$_3$, δ) 1.14 (s, 6 H), 1.17 (d, $J$ = 6.5 Hz, 3 H), 1.53 (m, 2 H), 1.57 (br s, 3 H), 1.68 (br s, 3 H), 1.95 (m, 2 H), 2.51 (AB q, 2 H), 3.50 (tq, $J$ = 6.5 Hz, 6.5 Hz, 1 H), 3.84 (s, 3 H), 5.08 (br t, $J$ = 7 Hz, 1 H); IR (film) 1756, 1729, 1630, 1463, 1437, 1356 cm$^{-1}$.

Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.11; H, 9.45.

**Method B. 2-Carbomethoxy-5,5-dimethyl-3-butylcyclopent-2-en-1-one (9).** A solution of 1.65 M *n*-butyllithium in hexane (1.21 mL, 2.0 mmol) was added dropwise to a suspension of CuI (190 mg, 1.0 mmol) in 10 mL of dry THF at −78 °C. After being stirred for 15 min the mixture became homogeneous and diester **3** (198 mg, 1.0 mmol) in 5 mL of dry THF was added dropwise. The mixture was stirred for 30 min at −78 °C, quenched with saturated $NH_4Cl$, and diluted with ether. The organic layer was dried and concentrated to provide 255 mg (99%) of diester **8**: 100-MHz $^1$H NMR (CDCl$_3$, δ) 0.90 (br t, 3 H), 1.22 (s, 6 H), 1.04–1.55 (band, 4 H), 1.95 (m, 2 H), 3.11 (s, 2 H), 3.69 (s, 6 H), 5.77 (s, 1 H).

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.90; H, 9.08.

A solution of 1.65 M *n*-butyllithium in hexane (0.710 mL, 1.17 mmol) was added dropwise to a solution of diisopropylamine (0.165 mL, 1.17 mmol) in 7 mL dry THF at 0 °C. The solution was stirred for 15 min at 0 °C and cooled to −78 °C whereupon a solution of diester **8** in 3 mL of dry THF was added dropwise. After 15 min at −78 °C the mixture was warmed to 25 °C over 30 min and quenched with 10% HCl and diluted with ether. The organic layer was washed with saturated $NaHCO_3$, dried, and concentrated. Flash chromatography (10% ethyl acetate/hexane) produced 100 mg (77%) of cyclopentenone **9** as a clear liquid: 100-MHz $^1$H NMR (CDCl$_3$, δ) 0.95 (br t, 3 H), 1.24 (s, 6 H), 1.20–1.75 (band 4 H), 2.55 (s, 2 H), 2.66 (m, 2 H), 3.86 (s, 3 H); IR (film) 1758, 1730, 1632, 1477, 1442 cm$^{-1}$.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.25; H, 8.73.

**2-Carbomethoxy-3,5,5-trimethylcyclopent-2-en-1-one (7)**: 100-MHz $^1$H NMR (CDCl$_3$, δ), 1.14 (s, 6 H), 2.41 (s, 3 H), 2.57 (s, 2 H), 3.85 (s, 3 H); IR (film) 1745, 1720, 1633, 1436, 1344 cm$^{-1}$.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.79; H, 7.86.

**3-(1-Buten-4-yl)-2-carbomethoxy-5,5-dimethylcyclopent-2-en-1-one (10)**: 100-MHz $^1$H NMR (CDCl$_3$, δ) 1.14 (s, 6 H), 2.36 (m, 2 H), 2.57 (s, 2 H), 2.90 (m, 2 H), 3.85 (s, 3 H), 5.06 (m, 2 H), 5.79 (m, 1 H); IR (film) 1756, 1722, 1632, 1443, 1368 cm$^{-1}$.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.89; H, 8.27.

**2-Carbomethoxy-5,5-dimethyl-3-ethylcyclopent-2-en-1-one (11)**: 100-MHz $^1$H NMR (CDCl$_3$, δ) 1.13 (s, 6 H), 1.27 (t, $J$ = 7 Hz, 3 H), 2.54 (s, 2 H), 2.73 (q, $J$ = 7 Hz, 2 H), 3.82 (s, 3 H); IR (film) 1760, 1732, 1639, 1447, 1365 cm$^{-1}$.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.11; H, 8.05.

**2-Carbomethoxy-5,5-dimethyl-3-[1-(2-dioxolanyl)prop-3-yl]cyclopent-2-en-1-one (12)**: 100-MHz $^1$H NMR (CDCl$_3$, δ) 1.14 (s, 6 H), 1.74 (m, 4 H), 2.57 (s, 2 H), 2.83 (m, 2 H), 3.84 (s, 3 H), 3.91 (m, 4 H), 4.88 (t, $J$ = 4 Hz); IR (film) 1758, 1726, 1618, 1434 cm$^{-1}$.

Anal. Calcd for $C_{15}H_{25}O_5$: C, 63.81; H, 7.85. Found: C, 63.58; H, 8.65.

**2-Carbomethoxy-5,5-dimethyl-3-isopropylcyclopent-2-en-1-one (13)**: 100-MHz $^1$H NMR (CDCl$_3$, δ) 1.14 (s, 6 H), 1.18 (d, $J$ = 7 Hz, 6 H), 2.52 (s, 2 H), 3.61 (m, 1 H), 3.85 (s, 3 H); IR (film) 1755, 1727, 1626, 1469, 1442 cm$^{-1}$.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.32; H, 8.65.

**2-Carbomethoxy-5,5-dimethyl-3-propen-1-ylcyclopent-2-en-1-one (15)**: 100-MHz $^1$H NMR (CDCl$_3$, δ) 1.17 (s, 6 H), 2.01 (dd, $J$ = 7 Hz, 1.5 Hz, 3 H), 2.71 (br s, 2 H), 3.87 (s, 3 H), 6.62 (dq, $J$ = 16 Hz, 7 Hz, 1 H), 7.31 (br d, $J$ = 16 Hz, 1 H); IR (film) 1703, 1630, 1572, 1243, 1226 cm$^{-1}$.

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.94; H, 7.70.

**2-Carbomethoxy-3-(2-methyl-2-hepten-6-yl)cyclopent-2-en-1-one (18)**: 100-MHz $^1$H NMR (CDCl$_3$, δ) 1.18 (d, $J$ = 7 Hz, 3 H), 1.51 (m, 2 H), 1.58 (br s, 3 H), 1.68 (br s, 3 H), 1.93 (m, 2 H), 2.57 (m, 4 H), 3.45 (m, 1 H), 3.85 (s, 3 H), 5.07 (br t, $J$ = 7 Hz, 1 H); IR (film) 1758, 1723, 1631, 1443, 1358 cm$^{-1}$.

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.58, H, 8.62.

**5-Carbo-*tert*-butoxy-3-isopropylcyclopent-2-en-1-one (17)**: 100-MHz $^1$H NMR (CDCl$_3$, δ) 1.22 (d, $J$ = 7 Hz, 3 H), 1.48 (s, 9 H), 2.65 (m, 3 H), 3.35 (dd, $J$ = 3 Hz, 6 Hz, 1 H), 5.88 (m, 1 H); IR (film) 1737, 1703, 1608, 1365 cm$^{-1}$.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61, H, 8.99. Found: C, 69.91, H, 9.22.

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**Registry No.** **3**, 90171-34-9; **4**, 86101-49-7; **7**, 91054-09-0; **8**, 91054-19-2; **9**, 91054-10-3; **10**, 91054-11-4; **11**, 91054-12-5; **12**, 91054-13-6; **13**, 91054-14-7; **14**, 91054-15-8; **15**, 91054-16-9; **17**, 91054-18-1; **18**, 91054-17-0; 3-dioxolan-2-ylpropylmagnesium bromide, 91083-05-5; methyl isobutyrate, 547-63-7; propargyl bromide, 106-96-7; $(CH_3)_2CuLi$, 15681-48-8; BuLi, 109-72-8; $CH_2{=}CHCH_2CH_2MgBr$, 7103-09-5; EtMgBr, 925-90-6; $(CH_3)_2CHMgCl$, 1068-55-9; $CH_2{=}CHCH_2MgCl$, 2622-05-1; *t*-BuOCO$(CH_2)_2C{\equiv}CCO_2CH_3$, 91054-07-8; $(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)MgCl$, 91054-08-9.

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# Synthesis of 9,10-Epoxy-9,10-secoabieta-8,11,13-triene[1]

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Of the several naturally occurring ring-B seco-tri- and tetracyclic diterpenoids which have been described in recent years, the simplest one is (+)-9,10-epoxy-9,10-secoabieta-8,11,13-triene (**1**) (Chart I) which was isolated in very small amount from the nonsaponifiable portion of Western White Pine bark.[2] As identification was based

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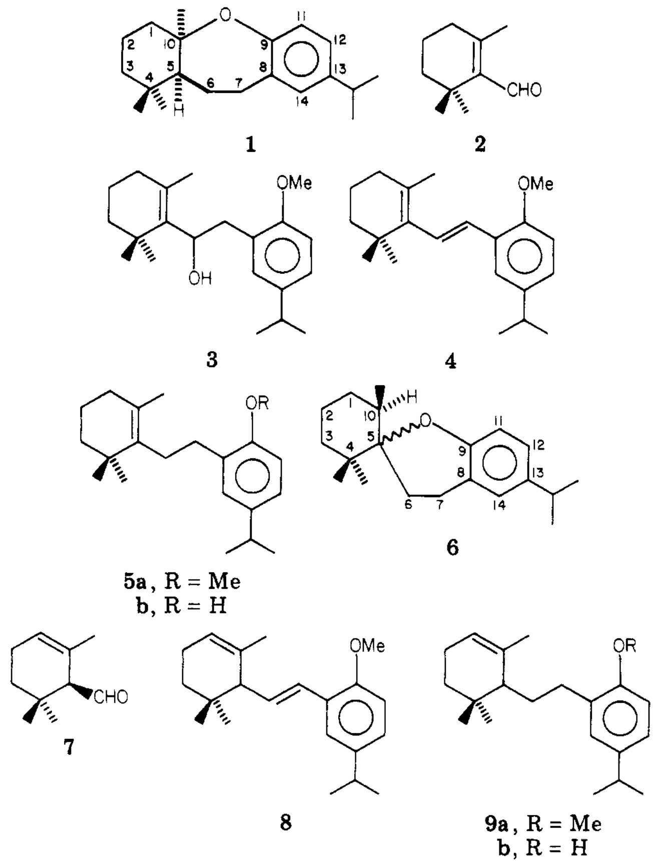
Chart I


1
2
3
4
5a, R = Me
b, R = H
6
7
8
9a, R = Me
b, R = H

only on spectroscopic evidence, an unambiguous synthesis of (±)-**1** was needed for comparison with the natural product. Such a synthesis is reported herewith.

Condensation of $\beta$-cyclocitral (**2**) with 2-methoxy-5-isopropylbenzyl chloride in the presence of sodium naphthalenide[3] afforded alcohol **3** in 46% yield. An attempt to effect hydrogenolysis of this allylic alcohol with dichloroaluminum hyride in ether resulted instead in dehydration of **4** (84%) which on catalytic reduction (Pd–C, ethyl acetate) gave a mixture of **5a** and two tetrahydro derivatives. However, exposure of **3** to triethylsilane–BF$_3$·O(Et)$_2$ at -10 °C[4,5] effected smooth conversion (69%) to **5a** which was demethylated (82%) to **5b** with thioethoxide in DMF.[6]

Cyclization of **5b** with BF$_3$·O(Et)$_2$ in CH$_2$Cl$_2$ at -20 °C for 2 h afforded two isomeric products in 63% and 8% yield. IR and NMR spectral Eu(fod)$_3$ shifts, MS, and GLC retention times of the major product were identical in all respects with those of the sample of (+)-**1** originally isolated from Western White Pine bark[8] and the $^{13}$C NMR spectrum (see Experimental Section) was consonant with the proposed structure. In the NMR spectrum of the minor product the shielded methyl singlet of **1** at $\delta$ 0.75 was replaced by a doublet at $\delta$ 0.99; consequently the substance was a 5,10-epoxy-9,10-secoabieta-8,11,13-triene. The partial stereochemistry **6** assigned to it was inferred from the lack of shielding of the C-10 methyl by the aromatic ring which indicated its axial orientation. This was confirmed by irradiation at the frequency of the methyl doublet which collapsed a one-proton quartet of triplets at $\delta$ 2.11 ($J$ = 7.5, 4.5 Hz) to a triplet ($J$ = 4.5 Hz). The signal in question was therefore that of H-10; the magnitude of its coupling constants to neighboring H-1$\alpha$,$\beta$ showed that it was equatorial.

Prolonged exposure of **1** to BF$_3$·OEt$_2$ resulted in quantitative conversion to **6**. Hence **1** is a kinetic and **6** is the thermodynamic product of cyclization. The stereochemistry at C-5 of **6** remains uncertain although a priori $\beta$-orientation of the C–O bond seems more likely. However, if this were so, one might, on the basis of models, expect some deshielding of the axial methyl on C-4 as compared with **1**; this was not observed. An attempt to distinguish between the two possibilities by using chemical shift reagents was unsuccessful because the substance failed to form a complex.

The same two products were isolated by cyclization of **9b** which was prepared from $\alpha$-cyclocitral (**7**) as follows. Wittig condensation of **7** with (2-methoxy-5-isopropylbenzyl)triphenylphosphonium chloride afforded **8** (69%). Subsequent catalytic hydrogenation (10% Pd–C, EtOH) to **9a** (84%) and demethylation of the latter gave **9b** (85%). Treatment of **9b** with BF$_3$·O(Et)$_4$ in the manner previously adopted for **5b** but for a somewhat longer period gave 17% of **1** and 52% of **6**.

## Experimental Section

IR spectra were recorded on neat samples on a Perkin-Elmer 257 spectrophotometer, $^1$H NMR spectra in CDCl$_3$ on a Bruker HX-270 spectrometer with Me$_4$Si as internal standard, and $^{13}$C NMR spectra at 67.89 MHz on the same instrument. High-resolution mass spectra were determined on an AEI MS-902 mass spectrometer, low-resolution mass spectra on a Finnigan 4510 GC/MS instrument at 70 eV. Precoated silica gel sheets (60F-254, 0.2 mm thick, EM reagent) were used for analytical TLC; preparative TLC was carried out on glass silica gel coated plates (60PF 254+366, EM reagent), layer thickness 1.5 mm. Silica gel (70–230 mesh; particle size 0.063–0.200 mm, EM reagent) was used for column chromatography.

**1-[2-(2-Methoxy-5-isopropylphenyl)-1-hydroxyethyl]-2,6,6-trimethylcyclohexene (3).** $\beta$-Cyclocitral was prepared from citral by cyclization to $\alpha$-cyclocitral (24%) and subsequent isomerization (64%)[8] or, more conveniently and in better yield (58%), by ozonolysis of $\beta$-ionone.[9]

To a mixture of 2.24 g of naphthalene and 0.460 g of small pieces of sodium in 15 mL of dry THF which had been stirred at room temperature for 1.5 h in a stream of N$_2$ was added a solution of 0.760 g of $\beta$-cyclocitral and 0.990 g of 2-methoxy-5-isopropylbenzyl chloride[10] in 5 mL of dry THF at -5 °C, which after 2 h was diluted with ether and then with aqueous NH$_4$Cl and extracted with ether. The washed and dried ether extract was evaporated at reduced pressure and purified by column chromatography to give 0.728 g (46%) of **3** as an oil: IR 3560, 1610, 1508, 1470, 1370, 1300, 1260, 1180, 1135, 1042, 825 cm$^{-1}$; NMR $\delta$ 1.01 and 1.10 (Me singlets), 1.23 ($d$, $J$ = 7 Hz, two Me doublets), 1.98 (vinyl Me singlet), 2.87 (septet, $J$ = 7 Hz, -C$H$(CH$_3$)$_2$), 2.92 ($dd$, $J$ = 13.5, 3.5 Hz), 3.13 ($dd$, $J$ = 13.5, 10 Hz, -C$H_2$CHOH), 3.82 (OMe), 4.48 ($dd$, $J$ = 10 and 3.5 Hz, -CH$_2$C$H$OH), 6.77 (d, $J$ = 8 Hz), 7.04 (d, $J$ = 2 Hz) and 7.07 (dd, $J$ = 8, 2 Hz, Ar protons); $M_r$ calcd for C$_{21}$H$_{32}$O$_2$ 316.2400, found (MS) 316.2403. Other major peaks in the low-resolution MS were at $m/z$ (relative intensity) 164 (100), 153 (42), 149 (66), 121 (9), 109 (25), 95 (14), 81 (6), and 69 (14).

**2-(2,6,6-Trimethyl-1-cyclohexenyl)-1-(2-methoxy-5-isopropylphenyl)ethane (5a).** (a) LiAlH$_4$ (46 mg) was added to a solution of 480 mg of anhydrous AlCl$_3$ in 5 mL of dry ether.

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After being stirred at room temperature for 1 h, a solution of 190 mg of **3** in 3 mL of dry ether was added dropwise with stirring. After 1 h the mixture was poured into ice-dilute HCl and extracted with ether. Evaporation of the washed and dried ether extract followed by column chromatography gave 150 mg (84%) of **4** as an oil: NMR $\delta$ 1.09 (two Me singlets), 1.26 (*d*, $J$ = 6 Hz, two Me doublets), 1.66 (m, two protons), 1.72 m (two protons), 1.79 (vinyl Me singlet), 2.04 (t, $J$ = 7 Hz, two protons), 2.88 (septet, $J$ = 7 Hz, $-CH(CH_3)_2$), 6.66 (br) and 7.33 (*d*, $J$ = 2 Hz, vinyl protons), 6.81 (*d*, $J$ = 8 Hz), 7.05 (dd, $J$ = 8, 2 Hz) and 7.33 (*d*, $J$ = 2 Hz, Ar protons); $M_r$ calcd for $C_{21}H_{30}O$ 298.2450, found (MS) 298.2448. Hydrogenation of 50 mg of **4** with 50 mg of 5% Pd–C in ethyl acetate for 5 h at room temperature, filtration, evaporation at reduced pressure, and preparative TLC furnished 32 mg (60%) of **5a** as an oil: IR 1610, 1585, 1495, 1460, 1258, 1130, 1055, 1028, 980, 945, 888, and 825 cm$^{-1}$; NMR $\delta$ 1.08 (two Me singlets), 1.26 (*d*, $J$ = 6 Hz, two Me doublets), 1.74 (vinyl Me), 1.50 (m), 1.60 (m), 1.97 (t, $J$ = 7 Hz), 2.25 (m), 2.65 (m, five two-protons multiplets), 2.86 (septet, $J$ = 7 Hz, $CH(CH_3)_2$), 3.82 (OMe), 6.79 (d, $J$ = 8 Hz), 6.87 (d, $J$ = 2 Hz), 6.87 (dd, $J$ = 8, 2 Hz, Ar protons); $M_r$ calcd for $C_{21}H_{32}O$, 300.2453, found (MS) 300.2449.

Other significant peaks in the low-resolution MS were at $m/z$ (relative intensity) 176 (24), 164 (60), 163 (100), 149 (18), 137 (13), 135 (15), 121 (7), 105 (12), 95 (13), 91 (11), and 81 (11). A minor fraction whose NMR spectrum exhibited two extra methyl doublets (relative intensity 2:1), no signals in the allylic proton regions other than the triplet of benzylic protons at $\delta$ 2.53, and no vinyl methyl signals was apparently a mixture of two tetrahydro derivatives but was not further characterized.

(b) A solution of 2.24 g of $BF_3{\cdot}O(Et)_2$ in 3 mL of $CH_2Cl_2$ was added at −10 °C to a solution of 1 g of **3** and 0.734 g of $Et_3SiH$ in 25 mL of $CH_2Cl$ with stirring. After 1 h of stirring at −10 °C, the mixture was diluted with ether, washed with water, dried, and evaporated. Purification of the residue by column chromatography gave 0.652 g (69%) of **5a** as an oil.

**2-(2,6,6-Trimethyl-1-cyclohexenyl)-1-(2-hydroxy-5-isopropylphenyl)ethane (5b).** A solution of 3.1 g of ethyl mercaptan in 30 mL of dry DMF was added to a suspension of 2.4 g of sodium hydride in 30 mL of dry DMF ($N_2$ atmosphere) and stirred for 5 min after which time a solution of 1.0 g of **5a** in 20 mL of dry DMF was added. The mixture was refluxed for 3 h, cooled, acidified with 10% HCl, and extracted with ether. Evaporation of the washed and dried ether extract followed by column chromatography furnished 0.39 g (82%) of **5b** as an oil: IR 3450, 1612, 1510, 1370, 1265, 1160, 1120, 900, 830, 775 cm$^{-1}$; NMR 1.08 (two Me singlets), 1.26 (*d*, $J$ = 6.5 Hz, two Me doublets), 1.73 (vinyl Me), 1.50 (m), 1.63 (m), 1.99 (t, $J$ = 7 Hz), 2.30 (m) and 2.66 (m, five two-proton multiplets), 2.86 (septet, $J$ = 7 Hz, $-CH(CH_3)_2$), 4.62 (br, OH), 6.69 (d, $J$ = 8 Hz), 6.94 (dd, $J$ = 8.2 Hz), 6.99 (d, $J$ = 2 Hz, Ar protons); $M_r$ calcd for $C_{20}H_{30}O$ 286.3397, found (MS) 286.2299.

**Cyclization of 5b.** A mixture of 0.10 g of **5b** and 0.18 mL of $BF_3{\cdot}O(Et)_2$ in 5 mL of $CH_2Cl_2$ was stirred at −20 °C for 2 h, poured into ice water, and extracted with ether. Evaporation of the washed and dried extract and preparative TLC of the residue gave 64 mg (63%) of (±)-**1** and 8 mg (8%) of (±)-**6**. The IR spectrum of (±)-**1** exhibited bands at 1500, 1462, 1385, 1252, 1219, 1162, 1125, 1110, 1050, 925, 905, 855, 845, and 826 cm$^{-1}$ and was identical with the IR spectrum of a sample of (+)-**1** supplied by Dr. J. W. Rowe; the $^1H$ NMR spectrum was superimposable on the NMR spectrum of (+)-**1** run under identical conditions as was the MS; $M_r$ calcd for $C_{20}H_{30}O$ 286.2296, found (MS) 286.2275. Other important peaks in the low-resolution MS were at $m/z$ (relative intensity) 243 (8), 215 (12), 202 (8), 189 (23), 162 (72), 150 (63), 149 (100), 137 (66), 135 (25), 123 (26), 121 (10), 109 (13), 105 (12), 95 (37), 90 (13), 81 (38), 79 (20), 69 (20), and 67 (13). The $^{13}C$ NMR spectrum of (±)-**1** had signals at $\delta$ 41.8 (t) and 42.2 (t) (C-1 and C-3), 20.6 (t) and 22.5 (t) (C-2 and C-6), 35.0 (s, C-4), 58.3 (d, C-5), 34.7 (t, C-7), 135.7 (s, C-8), 153.5 (s, C-9), 81.2 (s, C-10), 123.3 (d) and 124.3 (d) (C-11 and C-12), 143.5 (s, C-13), 127.1 (d, C-14), 33.4 (s, C-15), 24.2 (q, double intensity, C-16 and C-17), 33.0 (q, C-18), 21.4 (q) and 20.5 (q) (C-19 and C-20). The GLC retention times of (±)-**1** and (+)-**1** were also identical, 12.95 min (conditions Varian 2700 instrument, FID detector, OV-1 50-m capillary column, $N_2$ carrier gas, oven temperature 150–250 °C programmed at 10 °C/min).

Compound **6** exhibited $^1H$ NMR signals at $\delta$ 0.99 and 1.01 (two Me singlets), 0.99 (d, $J$ = 7.5 Hz, Me doublet), 1.21 (d, $J$ = 7 Hz, two Me doublets), 1.46 (m, 1 H), 1.58 (m, 2 H), 1.76 (m, 2 H), 1.95 (c, 2 H), 2.11 (tq, $J$ = 4.5, 7.5 Hz, H-10), 2.66 (m, 2 H, H-7), 2.80 (septet, $J$ = 7 Hz, $-CH(CH_3)_2$), 6.92 (d, $J$ = 8 Hz, H-11), 6.86 (br, H-14), 6.92 (d br, $J$ = 8 Hz, H-12); $M_r$ calcd for $C_{20}H_{30}O$ 286.2297, found (MS) 286.2297. Other significant peaks in the low-resolution MS were at $m/z$ (relative intensity) 243 (14), 215 (48), 202 (16), 189 (39), 173 (16), 162 (62), 150 (49), 149 (91), 137 (54), 123 (40), 1.07 (10), 95 (29), 91 (13), 81 (35), 79 (13), 69 (19), and 67 (12).

Exposure of synthetic **1** to $BF_3{\cdot}O(Et)_2$ for 4 h under the condition used for its preparation and workup in the usual fashion resulted in complete conversion to **6**.

**6-(2-Methoxy-5-isopropylstyryl)-1,5,5-trimethylcyclohexene (8).** A solution of 7 g of 2-methoxy-5-isopropylbenzyl chloride in 10.2 g of triphenylphosphine in dry benzene was refluxed for 6 h, cooled, and filtered. The precipitate was washed with dry benzene. Refluxing the filtrate for an additional 10 h furnished more salt: total yield 12.5 g (77%); mp 207–211 °C. To a suspension of 5.13 g of this material in 50 mL of dry benzene was added with stirring ($N_2$ atmosphere) 11.55 mL of a 12 M solution of *n*-BuLi in hexane. Stirring was continued at room temperature for 1.5 h, after which time a solution of 1.52 g of **7** in 10 mL of dry benzene was added at 0 °C. Stirring was continued at 0–5 °C for 4 h, the mixture was poured over ice–aqueous $NH_4Cl$, and extracted with ether. The extract was washed with saturated NaCl solution, dried, and evaporated; the residue was purified by column chromatography to give 2.05 g (69%) of **8** as an oil: IR 1605, 1498, 1465, 1252, 1125, 1040, 980, 825, 775 cm$^{-1}$; NMR $\delta$ 0.87 and 0.92 (two Me singlets), 1.22 (d, $J$ = 8 Hz, two Me doublets), 1.50 (m, 2 H), 1.62 (br, vinyl Me), 2.02 (m, 2 H), 2.27 (d br, $J$ = 9 Hz, H-6), 2.83 (septet, $-CH(CH_3)_2$), 2.79 (OMe), 5.42 (br, H-2), 3.99 (dd, $J$ = 16, 9 Hz), 6.67 (*d*, $J$ = 16 Hz, styryl protons), 6.79 (d, $J$ = 8 Hz), 7.02 (dd, $J$ = 8, 2 Hz), 7.37 (d, $J$ = 2 Hz, Ar protons); $M_r$ calcd for $C_{21}H_{30}O$ 298.2297, found (MS) 298.2312. Other significant peaks in the low-resolution MS were at $m/z$ (relative intensity) 242 (97), 227 (13), 199 (15), 163 (100), 133 (12), 107 (12), 93 (10), 91 (19), and 79 (10).

**2-(2,6,6-Trimethyl-2-cyclohexenyl)-1-(2-hydroxy-5-isopropylphenyl)ethane (9b).** A solution of 0.50 g of **8a** in 7 mL of EtOH was stirred with 50 mg of 10% Pd–C in an atmosphere of hydrogen, filtered after 40 min, evaporated, and purified by preparative TLC to give 0.42 g (84%) of **9a**: IR 1610, 1505, 1462, 1385, 1365, 1300, 1255, 1140, 1045, 895, 820 cm$^{-1}$; NMR $\delta$ 0.87 and 0.98 (two Me singlets), 1.21 (d, $J$ = 7.5 Hz, two Me doublets), 1.5 (c, 4–5 H), 1.68 (br, vinyl Me), 1.94 (m, 2 H), 2.61 (t, $J$ = 8 Hz, 2 H), 2.81 (septet, $-CH(CH_3)_2$), 3.77 (OMe), 5.27 (br, H-3), 6.75 (d, $J$ = 8 Hz), 6.97 (br), 6.99 (dd, $J$ = 8, 2 Hz, Ar protons); $M_r$ 300.2453, found (MS) 300.2438. Also seen in the low-resolution MS were peaks at $m/z$ (relative intensity) 176 (100) and 163 (93). A small fraction corresponding to a mixture of tetrahydro derivatives (NMR analysis) was also isolated.

Demethylation of 0.50 g of **9a** with thioethoxide as described for **5a** and column chromatography of the crude product gave 0.41 g (85%) of **9b** as an oil: IR 3400, 1610, 1505, 1450, 1260, 1220, 1115, 898, 830, 772 cm$^{-1}$; NMR $\delta$ 0.86 and 0.97 (two Me singlets), 1.19 (d, $J$ = 7 Hz, two Me doublets), 1.5 (c, 4–5 H), 1.67 (vinyl Me), 1.92 (m, 2 H), 2.60 (t, $J$ = 8 Hz, 2 H), 2.79 (septet, $-CH(CH_3)_2$), 5.29 (br, H-3), 6.65 (d, $J$ = 8 Hz), 6.90 (dd, $J$ = 8.2 Hz), 6.93 (d, $J$ = 2 Hz, Ar protons); $M_r$ calcd for $C_{20}H_{30}O$ 286.2297, found (MS) 286.2297. Other significant peaks were at $m/z$ (relative intensity) 162 (82), 150 (23), 149 (100), 147 (23), 137 (13), 123 (11), 107 (9), and 79 (8).

**Cyclization of 9b.** A solution of 0.10 g of **9b** and 0.18 mL of $BF_3{\cdot}O(Et)_2$ in 5 mL of $CH_2Cl_2$ was stirred at −20 °C for 3 h. Workup as described for **5b** gave 17 mg of **1** and 52 mg of **6**.

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