Stereoselective Cyclization assisted by the Selenyl Group. Biogenetic-type Synthesis in the *p*-Menthane Series

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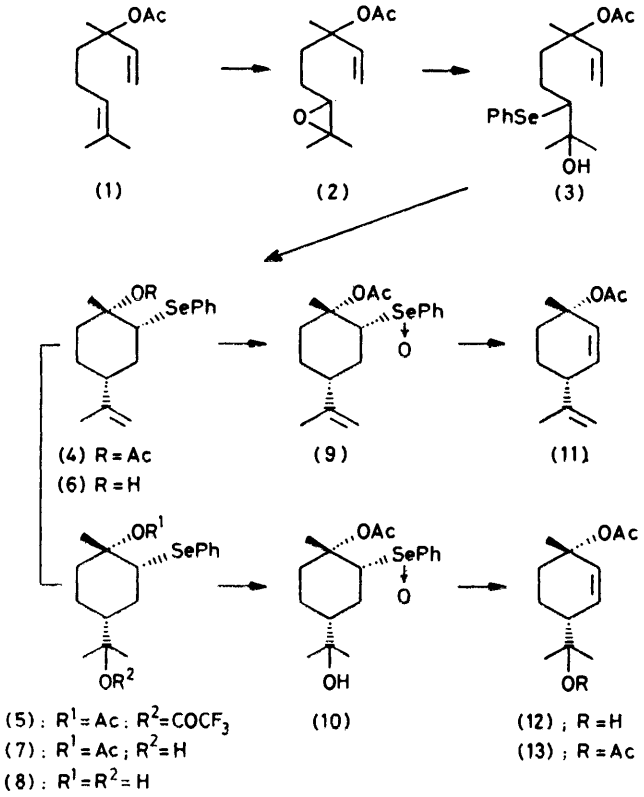
Acid-catalysed cyclisation of the β-hydroxyselenide (3), derived from linalyl acetate (1), afforded the *trans-p*-menthanes (4) and (5), the structures of which were confirmed by their transformation into (6), (11), (8), and (13), and alternative syntheses of these compounds. The structure determination of some products obtained by the reaction of limonene and α-terpineol epoxides with phenylselenium anion was also carried out.

NUMEROUS investigations concerning polyolefinic cyclisation, using a variety of reagents, have recently appeared in the literature.[1,2] As a result of our interest in the use of organoselenium compounds for the synthesis of natural products,[3,4] we reported a new selenium-assisted cyclisation reaction resulting in carbon–carbon bond formation,[4] and now report here a novel intramolecular rearrangement of the phenylselenyl group involved in stereoselective olefinic cyclisation.

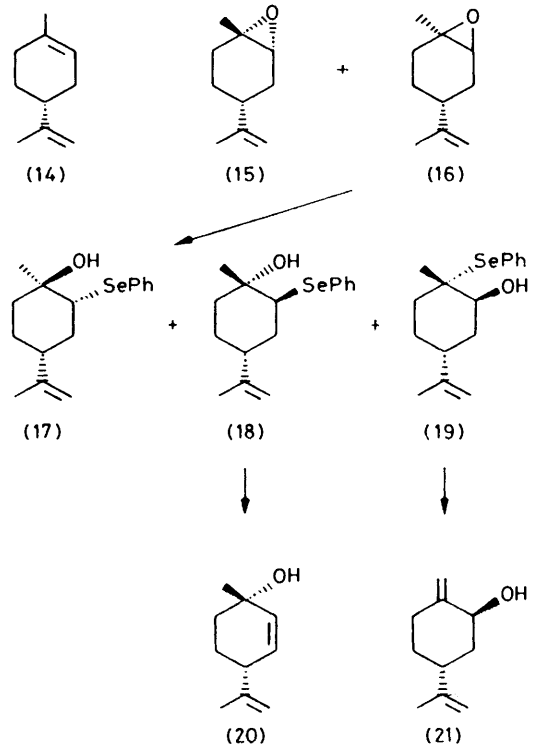
RESULTS AND DISCUSSION

The β-hydroxyselenide (3) prepared by epoxidation of linalyl acetate (1) using *m*-chloroperbenzoic acid followed



SCHEME 1

by treatment of the resulting epoxide (2) with phenylselenium anion,[5] was treated with trifluoroacetic acid in dichloromethane to give the cyclic compounds (4) and (5) in 6 and 36% yields, respectively. To confirm the structures of (4) and (5), these two compounds were converted into *trans-p*-mentha-2,8-dien-1-ol acetate (11) and *trans-p*-menth-2-ene-1,8-diol diacetate (13), respectively, as follows. The selenoxide (9), resulting from

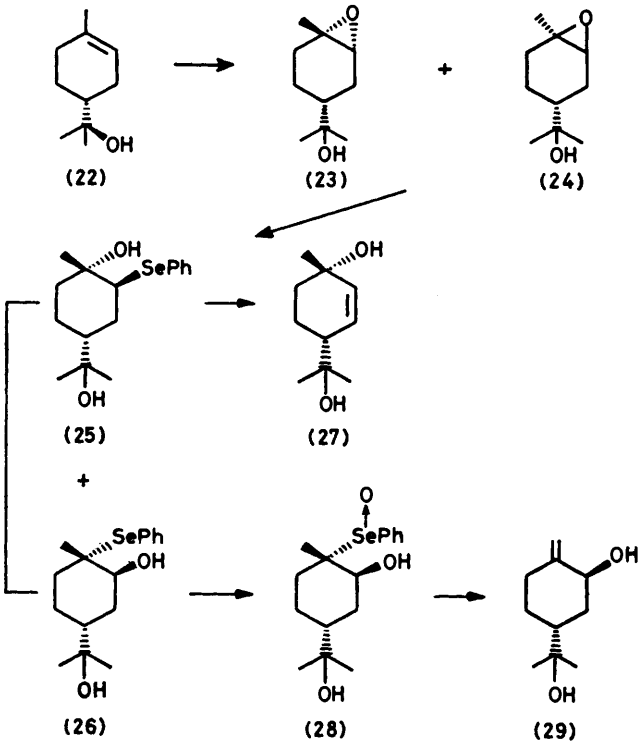


SCHEME 2

oxidation of (4) with 30% hydrogen peroxide, was heated in refluxing benzene to give (11). The monoacetate (7), obtained by partial hydrolysis of (5) with potassium carbonate in methanol, was similarly oxidised to the selenoxide (10); this on heating gave the monoacetate (12), which was acetylated to (13).

Alternative syntheses of (11) and (13) were also carried out. Firstly the stereoisomeric mixture of (15) and (16),[6] resulting from oxidation of limonene (14) with *m*-chloroperbenzoic acid, was treated with phenylselenium anion to afford (17), (18), and (19) in 1, 30, and 21% yields, respectively. Oxidation of compound (18)

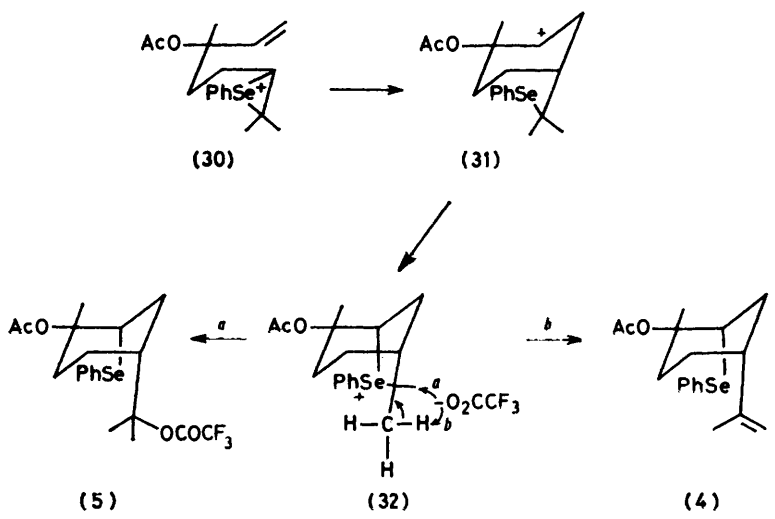
followed by elimination of the phenylselenyl group afforded compound (20), which was shown to be *trans-p*-mentha-2,8-dien-1-ol by comparison of the spectral data



SCHEME 3

with those of an authentic sample.[7] Acetylation of (20) gave the acetate (11), which was identical to the compound (11) derived by cyclisation of (3) as already described. Spectral comparison demonstrated that the selenide alcohol (6), derived by hydrolysis of acetate (4), was not identical to compound (18). These results indicated that the relative configuration of methyl and isopropenyl groups in (4) and (18) was the same, while the relationship between these and the phenylselenyl group was different. Thus, the structure of compound (4) was determined to be as shown in Scheme 1. Furthermore, compound (19) was converted into *trans-p*-mentha-1(7),8-dien-2-ol (21), the spectroscopic data of which were identical to those of an authentic sample.[7] Secondly, the stereoisomeric mixture of epoxides (23) and (24), prepared by oxidation of α-terpineol (22) with *m*-chloroperbenzoic acid, was treated with phenylselenium anion [5] to give compounds (25) and (26) in 64 and 13% yield, respectively. Compound (27), obtained from compound (25) by oxidation with 30% hydrogen peroxide, followed by thermolysis, was shown not to be *cis-p*-menth-2-ene-1,8-diol [8] (by comparison of the spectroscopic data), but found to be *trans-p*-menth-2-ene-1,8-diol. The diacetate (13), prepared by acetylation of compound (27), was identical to the compound (13) derived by cyclisation of (3) as already described. The selenide alcohol (8), obtained by hydrolysis of the acetate (7), was not identical to compound (25). These results suggested that the structure of compound (5) is as shown in Scheme 1. Furthermore, compound (26) was converted into *trans-p*-menth-1(7)-ene-2,8-diol (29), through the selenoxide (28) by the procedure described above, which was shown to be identical to an authentic sample [9] by comparison of the spectroscopic data.

Thus we have confirmed the stereochemistry of the products (4) and (5) resulted from acid-catalysed cyclisation of the β-hydroxyselenide (3). The formation of (4) and (5) in this reaction may be explained by the reaction mechanism outlined in Scheme 4. Thus, the



SCHEME 4

pound (11) derived by cyclisation of (3) as already described. Spectral comparison demonstrated that the selenide alcohol (6), derived by hydrolysis of acetate (4), was not identical to compound (18). These results indicated that the relative configuration of methyl and isopropenyl groups in (4) and (18) was the same, while the relationship between these and the phenylselenyl group was different. Thus, the structure of compound (4) was determined to be as shown in Scheme 1. Furthermore, compound (19) was converted into *trans-p*-mentha-1(7),8-dien-2-ol (21), the spectroscopic data of which were identical to those of an authentic sample.[7] Secondly, the stereoisomeric mixture of epoxides (23) and (24), prepared by oxidation of α-terpineol (22) with *m*-chloroperbenzoic acid, was treated with phenylselenium anion [5] to give compounds (25) and (26) in 64 and 13% yield, respectively. Compound (27), obtained from compound (25) by oxidation with 30% hydrogen peroxide, followed by thermolysis, was shown not to be *cis-p*-menth-2-ene-1,8-diol [8] (by comparison of the spectroscopic data), but found to be *trans-p*-menth-2-ene-1,8-diol. The diacetate (13), prepared by acetylation of compound (27), was identical to the compound (13) derived by cyclisation of (3) as already described. The selenide alcohol (8), obtained by hydrolysis of the acetate (7), was not identical to compound (25). These results suggested that the structure of compound (5) is as shown in Scheme 1. Furthermore, compound (26) was converted into *trans-p*-menth-1(7)-ene-2,8-diol (29), through the selenoxide (28) by the procedure described above, which was shown to be identical to an authentic sample [9] by comparison of the spectroscopic data.

Thus we have confirmed the stereochemistry of the products (4) and (5) resulted from acid-catalysed cyclisation of the β-hydroxyselenide (3). The formation of (4) and (5) in this reaction may be explained by the reaction mechanism outlined in Scheme 4. Thus, the selenium cation (32), generated by intramolecular rearrangement of the olefinic group in the seleniranium ion (30), followed by intramolecular rearrangement to (31), is substituted by the trifluoroacetoxy-group

(path *a*) to give compound (5), and deprotonated by the trifluoroacetoxy-group (path *b*) to afford compound (4).

EXPERIMENTAL

I.r. spectra were obtained with a Hitachi 215 spectrometer, n.m.r. spectra with a JEOL-PMX-60 (tetramethylsilane as internal reference), and mass spectra with Hitachi M-52G and JEOL-JMS-01SG-2 spectrometers. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected.

6,7-*Epoxylinalyl Acetate* (2).—To a stirred solution of linalyl acetate (1) (2.0 g, 10.2 mmol) in dichloromethane (25 ml) and saturated sodium hydrogencarbonate solution (25 ml) was added *m*-chloroperbenzoic acid (2.1 g, 12.2 mmol). After stirring for 14 h at room temperature, the dichloromethane layer was washed with saturated sodium chloride solution and dried (Na_2SO_4). Removal of the solvent afforded a crude product which was chromatographed on silica gel (50 g) using hexane–ethyl acetate (9 : 1) as eluant to give *epoxide* (2) (2.0 g, 92%) as a colourless oil (Found: C, 67.9; H, 9.75. $C_{12}H_{20}O_3$ requires C, 67.9; H, 9.5%); $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1} (C=O); δ($CDCl_3$) 1.27, 1.3 (6 H, each s, Me), 1.57 (3 H, s, Me), 2.03 (3 H, s, OAc), 2.73 (1 H, t, *J* 9 Hz, C-6–H), and 5.0—6.4 (3 H, m, olefinic protons); *m/e* 153 ($M^+ - 59$).

6-*Acetoxy*-2-*hydroxy*-2,6-*dimethyl*-3-*phenylseleno*-*octa*-7-*ene* (3).—To a suspension of diphenyl diselenide (3.89 g, 12.5 mmol) in ethanol (70 ml) was added sodium borohydride (784 mg, 20.8 mmol) in small portions with stirring at 0 °C under an atmosphere of nitrogen. After stirring for 30 min, a solution of epoxide (2) (4.4 g, 20.8 mmol) in ethanol (70 ml) was added and the reaction mixture stirred for 3 h at room temperature. The reaction mixture was then poured into saturated sodium chloride solution (100 ml) and extracted with ether. The ethereal extract was washed with saturated sodium chloride solution and dried (Na_2SO_4). Removal of the solvent afforded a yellow oil which was chromatographed on silica gel (140 g) using hexane–ethyl acetate (5 : 1) as eluant to give *selenide* (3) (5.84 g, 86%) as a colourless oil (Found: C, 58.85; H, 7.1. $C_{18}H_{26}O_3Se$ requires C, 58.55; H, 7.1%); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH) and 1 720 cm^{-1} (C=O); δ (CCl_4) 1.30, 1.37 (6 H, each s, Me), 1.56 (3 H, s, Me), 2.03 (3 H, s, OAc), and 5.6—6.35 (3 H, m, olefinic protons); *m/e* 368/370 (M^+).

Reaction of (3) *with Acid Catalyst.*—To a solution of selenide (3) (3.7 g, 10 mmol) in dry dichloromethane (200 ml) at 0 °C was added trifluoroacetic acid (12 ml) under an atmosphere of nitrogen. After stirring for 30 min at 0 °C, the reaction mixture was poured into water (100 ml). The dichloromethane layer was washed with saturated sodium hydrogencarbonate solution, saturated sodium chloride solution, and dried (Na_2SO_4). Removal of the solvent afforded a crude product which was chromatographed on silica gel (80 g) using hexane–ethyl acetate (24 : 1) as eluant to give the *p*-menthanes (4) (220 mg, 6%) and (5) (1.7 g, 36%): for compound (4) (Found: C, 61.65; H, 7.0. $C_{18}H_{24}O_2Se$ requires C, 61.55; H, 6.9%); $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1} (C=O); δ(CCl_4) 1.7br (3 H, s, Me), 1.73 (3 H, s, Me), 2.0 (3 H, s, OAc), 4.73br (2 H, s, olefinic protons), and 7.1—7.8 (5 H, m, aromatic); *m/e* 350/352 (M^+): for compound (5) (Found: C, 52.05; H, 5.45. $C_{20}H_{25}O_4F_3Se$ requires C, 51.65; H, 5.45%); $\nu_{max.}$ ($CHCl_3$) 1 780 ($CO{\cdot}CF_3$) and 1 730 cm^{-1} (C=O); δ(CCl_4) 1.52 (6 H, s, 2 × Me), 1.75 (3 H, s, Me), 2.0 (3 H, s, OAc), and 7.1—7.8 (5 H, m, aromatic protons); *m/e* 464, 466 (M^+).

1α-*Hydroxy*-2α-*phenylseleno*-trans-p-*menth*-8-*ene* (6).—A solution of the acetate (4) (65 mg) and potassium hydroxide (11.4 mg) in ethanol (15 ml) was refluxed for 2 h. The reaction mixture was neutralised with 10% hydrochloric acid and extracted with ethyl acetate. The organic extract was washed with saturated sodium chloride solution and dried (Na_2SO_4). Removal of the solvent afforded a crude product which was chromatographed on silica gel (1 g) using hexane–ethyl acetate (19 : 1) as eluant to give the *alcohol* (6) (52 mg, 90.9%) as a colourless oil (Found: C, 60.95; H, 7.25. $C_{16}H_{22}OSe{\cdot}0.2H_2O$ requires C, 61.4; H, 7.25%); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ(CCl_4) 1.25 (3 H, s, Me), 1.67br (3 H, s, Me), 4.58br (2 H, s, olefinic protons), and 7.1—7.8 (5 H, m, aromatic); *m/e* 308, 310 (M^+).

1α-*Acetoxy*-2α-*phenylseleno*-trans-p-*menthan*-8-*ol* (7).—To a stirred solution of trifluoroacetate (5) (231 mg, 0.497 mmol) in methanol (10 ml) at 0 °C was added potassium carbonate (71 mg, 0.514 mmol). After stirring for 1 h at room temperature, water (10 ml) was added to the reaction mixture, which was then extracted with ether. The ethereal extract was washed with saturated sodium chloride solution and dried (Na_2SO_4). Evaporation of the solvent afforded a crude product which was chromatographed on silica gel (6 g) using hexane–ethyl acetate (4 : 1) as eluant to give, after precipitation from hexane, the *alcohol* (7) (175 mg, 95.5%) as a powder (Found: C, 57.9; H, 6.95. $C_{18}H_{26}O_3Se{\cdot}0.2H_2O$ requires C, 57.95; H, 7.15%); $\nu_{max.}$ ($CHCl_3$) 3 600 (OH) and 1 720 cm^{-1} (C=O); δ(CCl_4) 1.08 (6 H, s, 2 × Me), 1.72 (3 H, s, Me), 2.0 (3 H, s, OAc), and 7.1—7.8 (5 H, m, aromatic); *m/e* 368/370 (M^+).

1α-*Hydroxy*-2α-*phenylseleno*-trans-p-*menthan*-8-*ol* (8).—The compound (8) was obtained from (7), by the same procedure as for the preparation of (6), in 91.9% yield as a colourless oil (Found: M^+, 328.0903. $C_{16}H_{24}O_2Se$ requires *M*, 328.0940); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ(CCl_4) 1.10 (6 H, s, 2 × Me), 1.25, (3 H, s, Me), 3.20 (1 H, dd, *J* 4, 12 Hz, C-2–H), and 7.1—7.8 (5 H, m, aromatic).

1-*Acetoxy*-trans-p-*mentha*-2,8-*diene* (11).—To a stirred solution of (4) (96 mg) in tetrahydrofuran (0.5 ml) at 0 °C was added 30% hydrogen peroxide (0.5 ml). After stirring for 20 min at 0 °C, the reaction mixture was diluted with water (5 ml) and extracted with ether. The ethereal extract was washed with saturated sodium chloride solution and dried (Na_2SO_4). Removal of the solvent gave the crude material (9) (88 mg) which was used without further purification. A solution of the above product (9) (85 mg) in benzene (20 ml) was refluxed for 1 h. Removal of the benzene and chromatography of the residue on neutral alumina (grade III, 4 g) using hexane–ethyl acetate (98 : 2) as eluant afforded the *olefin* (11) [37.5 mg, 70.2% from (4)] as a colourless oil (Found: C, 72.8; H, 9.35. $C_{12}H_{18}O_2{\cdot}0.2H_2O$ requires C, 72.85; H, 9.35%); $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1} (C=O); δ(CCl_4) 1.57 (3 H, s, Me), 1.77br (3 H, s, Me), 1.98 (3 H, s, OAc), 2.77 (1 H, m, C-4–H), 4.87br (2 H, s, olefinic protons), 5.78 (1 H, dd, *J* 10, 2 Hz, olefinic proton), and 6.30 (1 H, dd, *J* 10, 1 Hz, olefinic proton); *m/e* 135 ($M^+ - 59$).

1α-*Acetoxy*-trans-p-*menth*-2-*en*-8-*ol* (12).—The compound (12) was obtained from (7), by the procedure described above, in 71% yield as a colourless oil (Found: C, 66.4; H, 9.3. $C_{12}H_{20}O_3{\cdot}0.3H_2O$ requires C, 66.2; H, 9.55%); $\nu_{max.}$ ($CHCl_3$) 3 600 (OH) and 1 720 cm^{-1} (C=O); δ(CCl_4) 1.1, 1.17 (6 H, each s, 2 × Me), 1.50 (5 H, s, Me), 1.90 (3 H, s, OAc), and 5.82—6.47 (2 H, m, olefinic protons); *m/e* 153 ($M^+ - 59$).

1,8-*Diacetoxy*-trans-p-*menth*-2-*ene* (13).—To a solution of (12) in pyridine (0.5 ml) was added acetic anhydride (30 mg) and the mixture stirred for 14 h at room temperature. The reaction mixture was poured into water (3 ml) and extracted with ether. The ethereal extract was washed with saturated sodium chloride solution and dried (Na_2SO_4). Removal of the solvent afforded a crude product which was chromatographed on neutral alumina (grade III, 2 g) using hexane–ethyl acetate (9 : 1) as eluant to give *diacetate* (13) (42 mg 58%) as a colourless oil (Found: C, 65.85; H, 8.8. $C_{14}H_{22}O_4$ requires C, 66.1; H, 8.8%); $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1} (C=O); δ(CCl_4) 1.38 (6 H, s, 2 × Me), 1.51 (3 H, s, Me), 1.9, 1.95 (6 H, each s, 2 × OAc), 2.87 (1 H, m, C-4–H), 5.73 (1 H, dd, *J* 10, 2 Hz, olefinic proton), and 6.28 (1 H, dd, *J* 10, 1 Hz); *m/e* 195 ($M^+ - 59$).

Epoxidation of D-*Limonene* (14).—Epoxidation of D-limonene (14), by the procedure described for (1), gave the *trans*-epoxide (15) and *cis*-epoxide (16) as a 1 : 1 mixture. These products were used without separation.

Reaction of Epoxides (15) *and* (16) *with Phenylselenium Anion.*—Treatment of the mixture of (15) and (16) with phenylselenium anion was carried out following the same procedure described for (2), to give 1β-hydroxy-2α-phenylseleno-*cis*-*p*-menth-8-ene (17) (1%), 1α-hydroxy-2β-phenylseleno-*trans*-*p*-menth-8-ene (18) (30%), and 2β-hydroxy-1α-phenylseleno-*trans*-*p*-menth-8-ene (19) (21%). Compound (17); δ(CCl_4) 1.33 (3 H, s, Me), 1.73br (3 H, s, Me), 3.1br (1 H, s, C-2–H), 4.76br (2 H, s, olefinic protons), and 7.1—7.8 (5 H, m, aromatic); *m/e* 308/310 (M^+). Compound (18) (Found: C, 62.25; H, 7.35. $C_{16}H_{22}OSe$ requires C, 62.15; H, 7.15%); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ(CCl_4) 1.36 (3 H, s, Me), 1.66br (3 H, s, Me), 3.38br (1 H, s, C-2–H), 4.75br (2 H, s, olefinic), and 7.1—7.8 (5 H, m, aromatic); *m/e* 308/310 (M^+). Compound (19) (Found: C, 61.45; H, 7.05. $C_{16}H_{22}OSe{\cdot}0.2H_2O$ requires C, 61.4; H, 7.25%); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ(CCl_4) 1.30 (3 H, s, Me), 1.75br (3 H, s, Me), 3.88br (1 H, s, C-2–H), 4.77br (2 H, s, olefinic), and 7.1—7.8 (5 H, m, aromatic); *m/e* 308/310 (M^+).

trans-p-*Mentha*-2,8-*dien*-1-*ol* (20).—To a stirred solution of (18) (382 mg) in tetrahydrofuran (4 ml) at 0 °C was added 30% hydrogen peroxide (1 ml). After stirring for 20 min at 0 °C, tetrahydrofuran (20 ml) and pyridine (1 ml) were added to the reaction mixture. The reaction mixture was then refluxed for 1 h. After evaporation of the solvent, water (10 ml) was added to the residue and the resulting mixture was extracted with ethyl acetate. The combined extracts were washed with saturated sodium chloride solution and dried (Na_2SO_4). Removal of the solvent and chromatography of the residue on silica gel (5 g) using hexane–ethyl acetate (1 : 1) as eluant gave the olefin (20) (133 mg, 70.8%) as a colourless oil (Found: M^+, 152.1198. $C_{10}H_{16}O$ requires *M*, 152.1200); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ(CCl_4) 1.22 (3 H, s, Me), 1.75br (3 H, s, Me), 4.78br (2 H, s, olefinic), and 5.67br (2 H, s, olefinic).

p-*Mentha*-1,8-*dien*-trans-2-*ol* (21).—The compound (21) was obtained from (19) by the procedure described above in 70.3% yield as a colourless oil (Found: M^+, 152.1190. $C_{10}H_{16}O$ requires *M*, 152.1200); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ(CCl_4) 1.7br (3 H, s, Me), 4.25 (1 H, distorted t, C-2–H), and 4.65 (4 H, br s, olefinic).

Epoxidation of α-*Terpineol* (22).—Epoxidation of α-terpineol (22) was carried out, following the procedure described for (1), to give a mixture of *trans*- (23) and *cis*-epoxide (24). These products were used without separation.

Reaction of Epoxides (23) *and* (24) *with Phenylselenium Anion.*—Treatment of a mixture of (23) and (24) with phenylselenium anion, following the procedure described for (2), gave 1α-hydroxy-2β-phenylseleno-*trans*-*p*-menthan-8-ol (25) (64%) as a colourless oil, and 2β-hydroxy-1α-phenylseleno-*trans*-*p*-menthan-8-ol (26) (13%) as a powder. Compound (25) (Found: M^+, 328.0922. $C_{16}H_{24}O_2Se$ requires *M*, 328.0940): $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ(CCl_4) 1.07 (6 H, s, 2 × Me), 1.34 (3 H, s, Me), 3.43 (1 H, br s, C-2–H), and 7.1—7.8 (5 H, m, aromatic protons): compound (26) (Found: C, 58.15; H, 7.45. $C_{16}H_{24}O_2Se{\cdot}0.2H_2O$ requires C, 58.05; H, 7.45%); $\nu_{max.}$ (KBr) 3 300 cm^{-1} (OH); δ($CDCl_3$) 1.25 (6 H, s, 2 × Me), 1.37 (3 H, s, Me), 4.0br (1 H, s, C-2–H), and 7.2—7.8 (5 H, m, aromatic); *m/e* 326/328 (M^+).

trans-p-*Menth*-2-*ene*-1,8-*diol* (27).—The compound (27) was obtained from (25), by the procedure described above for (18), as colourless needles in 74% yield, m.p. 91—92 °C (recrystallisation from benzene) (Found: C, 70.25; H, 10.85. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.65%); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ(CCl_4) 1.17 (3 H, s, Me), 1.22 (6 H, s, 2 × Me), and 5.82br (2 H, s, olefinic); *m/e* 152 ($M^+ - 18$).

trans-p-*Menth*-1-*ene*-2,8-*diol* (29).—The compound (29) was obtained from (26), by the procedure described for (18), in 82% yield as colourless *needles*, m.p. 109—110 °C (recrystallisation from benzene) (Found: C, 70.4; H, 10.9. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.65%); $\nu_{max.}$ ($CHCl_3$) 3 600 cm^{-1} (OH); δ($CDCl_3$) 1.17 (6 H, s, 2 × Me), 4.37 (1 H, t, *J* 3 Hz, C-2–H), and 4.75 (2 H, m, olefinic); *m/e* 152 ($M^+ - 18$).

1-*Acetoxy*-trans-p-*mentha*-2,8-*diene* (11).—The compound (11) was obtained from (20) by the procedure described for (12), in 56% yield as a colourless oil, which was identical to the sample obtained from (9) by i.r. ($CHCl_3$) and n.m.r. (CCl_4) spectral comparison.

1,8-*Diacetoxy*-trans-p-*menth*-2-*ene* (13).—Compound (13) was obtained from (27), by the procedure described for (12), in 47% yield as a colourless oil, which was identical to the sample obtained from (12) by i.r. ($CHCl_3$) and n.m.r. (CCl_4) spectral comparison.

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