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INTRAMOLECULAR REACTIONS OF ALLYLOXY RADICALS

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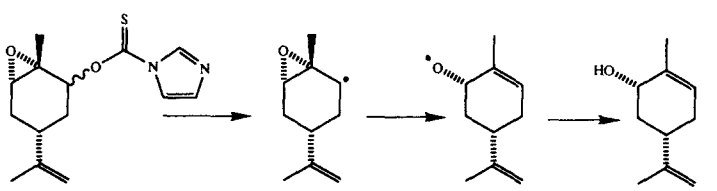
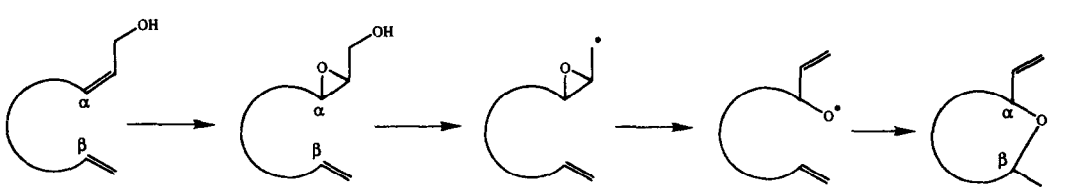
Allyloxy radicals, formed by epoxide cleavage, have cyclised onto appropriately positioned alkenes to form tetrahydrofurans, and the diastereoselectivity of the cyclisation has been studied. The reaction was used to synthesise lilac alcohols which were then used to confirm the stereochemistry of such cyclisations.

The occurrence of tetrahydrofurans in secondary metabolites is widespread, and so a great effort has been directed towards producing syntheses of tetrahydrofurans[1] which feature stereochemical control.[2] In a report by Barton, Motherwell and Motherwell[3] featuring the synthesis of cis-carveol (4) from the epoxide (1), a by-product (5) was mentioned which occurred in varying amounts depending on the conditions of the reaction. Conditions were found which maximised the yield of (4) and minimised the yield of the bicyclic product. We were intrigued by the formation of the tetrahydrofuran



(1) (2) (3) (4)

(5)



(6) (7) (8) (9) (10)

SCHEME 1

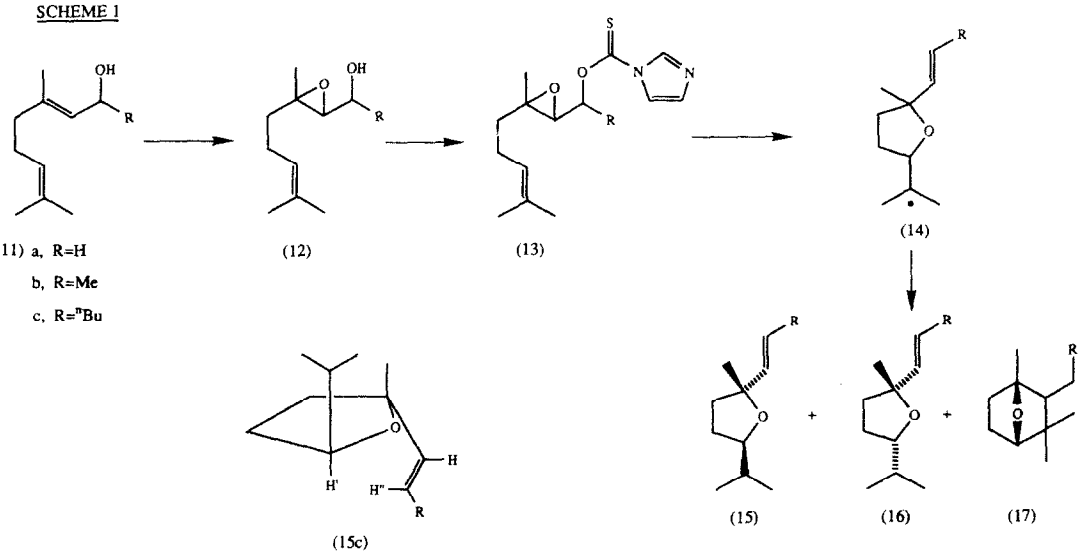
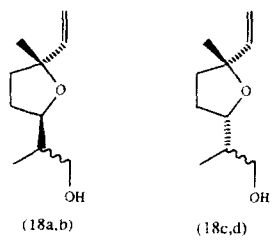


TABLE A

STARTING EPOXIDE	REACTION PRODUCT YIELDS		
(12)	(15)	(16)	(17)
a	10%	4%	0%
b	48%	8%	14%
c	56%	7%	22%



(18a,b) (18c,d)

(5) and wondered whether similar tetrahydrofurans could be formed in synthetically useful yields using neutral radical methods and also to what extent such cyclisations (8)→(10) might be diastereoselective. The bicycle (5) features two methyl groups on the cyclisation terminus and so does not report on the diastereoselectivity of the cyclisation. Since molecules like (8) can be derived from allylic alcohols (6), the stereochemistry at Cα is totally controllable using the chiral epoxidation approach of Sharpless.[4] If the cyclisation to (10) were fully diastereoselective, this would lead to complete control of stereochemistry at Cβ also, resulting in a highly desirable route to tetrahydrofurans.

A. Synthesis of 2,2,5-trisubstituted tetrahydrofurans. (Scheme 1)

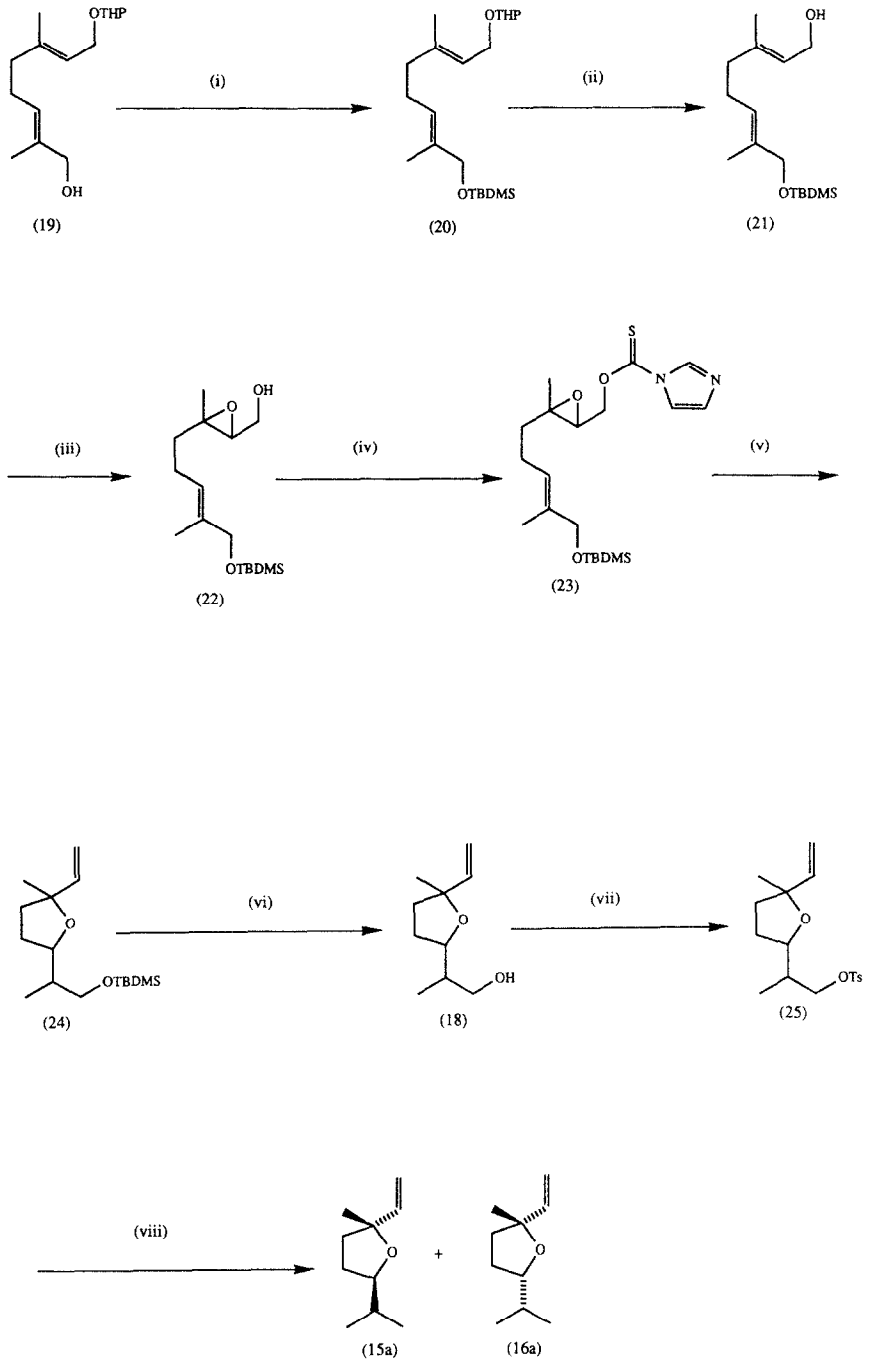
Geraniol (11a) and the products (11b) and (11c), derived from addition of methyl lithium and n-butyl lithium to citral, were regioselectively epoxidised using the Sharpless vanadium technology.[5] Reaction with thiocarbonyl diimidazole in dichloromethane gave rise to clean conversion to the thiocarbonylimidazolide (13). This compound was not isolated and the completeness of the conversion was judged by n.m.r. On reaction with tributyltin hydride and AIBN, two monocyclic tetrahydrofuran products (15) and (16) and the bicyclic compound (17) were produced in the yields shown. The bicyclic compound results from further reaction of the intermediate (14). What is immediately apparent is that the case where R=H produces anomalously low yields; further investigation revealed that these products are very volatile, much more so than for R=Me or Bu.

The monocyclic tetrahydrofuran isomers were separable for R=n-Bu and so we decided to determine the stereochemistry of the major and minor products for this case. For the major compound, irradiation of H' led to a 4% enhancement of H , showing that H' and the hexenyl side-chain must be cis on the tetrahydrofuran ring as in (15c). No such enhancement was seen for the other isomer. We have been reluctant to rely on this Overhauser evidence to indicate the relative stereochemistry of the tetrahydrofurans, so below we have performed a chemical correlation for the case, R=H.

B. Synthesis of lilac alcohols. (Scheme 2)

Lilac alcohols (18a-d) are fragrant oils first isolated from Syringa vulgaris by Wakayama and Namba.[6] We have noted three syntheses of these compounds.[7] The four diastereoisomers of lilac alcohol are all separable by gas-liquid chromatography and the stereochemistry of each has been assigned. The lilac alcohols are thus ideal synthetic targets for this work since the

SCHEME 2



REAGENTS: (i) TBDMSCl, DBU, CH_2Cl_2; (ii) $MgBr_2.Et_2O$; (iii) ^tBuOOH, $VO(acac)_2$, PhH ;(iv) N,N'-thiocarbonyl diimidazole, CH_2Cl_2; (v) $^nBu_3SnH$, AIBN, THF; (vi) $^nBu_4N^+F^-$, THF; (vii) TsCl, C_5H_5N; (viii) $LiAlH_4$, Et_2O

stereochemistry of the products can be determined by comparison with authentic material.

The diol derivative (20) was made by converting geraniol to its tetrahydropyranyl ether, oxidizing with selenium dioxide[8] and then converting the newly produced alcohol function to its tert-butyldimethylsilyl ether. Selective deprotection of the tetrahydropyranyl group was then achieved using magnesium bromide etherate. Treatment of this compound (21) with vanadyl-acetylacetonate and tert-butylhydroperoxide caused selective epoxidation to give (22); this was treated sequentially with thiocarbonyl diimidazole and then tributyltin radicals. Four tetrahydrofurans were produced in ratio 5:5:2:1. Treatment with tetra-n-butylammonium fluoride then gave the lilac alcohols. G.l.c. comparison with authentic samples using co-injection confirmed that the major isomers were indeed the trans isomers i.e. (18a) and (18b) while the minor components were the cis lilac alcohols (18c) and (18d).

The lilac alcohols were now used to investigate the stereochemistry of the cyclisation products (15a) and (16a). If the n.m.r. data (using the n.O.e. effect as mentioned above) on (15c) and (16c) are correct, then the trans isomer (15a) would be expected to be the major product, and (16a) the minor. An 8:1 mixture of trans:cis lilac alcohols (18a/b:18c/d) was converted to the corresponding tosylates which led to an 8:1 mixture of two tetrahydrofurans on treatment with lithium aluminium hydride. Spectroscopic comparison showed that the major product corresponded to the major product from the geraniol derivative cyclisation. (Likewise for the minor product from both reactions). So, as expected, the major product featured a trans-disposition of the two largest alkyl groups.

C. Synthesis of 2,5-disubstituted tetrahydrofurans. (Scheme 3)

The above studies have all led to the synthesis of 2,2,5-trisubstituted tetrahydrofurans. Whereas these substrates were conveniently synthesised, any wish to produce tetrahydrofurans stereoselectively should be directed to the synthesis of 2,5-disubstituted tetrahydrofurans. Accordingly the three molecules (32a-c) were synthesised from butane-1,4-diol using the methods shown in Scheme 3. Compounds (32b) and (32c) were produced by addition of methyl lithium and n-butyl lithium respectively to aldehyde (33). Cyclisations with tributyltin radicals were effected as before with the results indicated in the table. As is apparent, the syntheses of 2,5-disubstituted tetrahydrofurans are only moderately stereoselective. A forthcoming paper will contrast this with the stereoselection obtainable in 6-membered ring synthesis.

ACKNOWLEDGEMENTS

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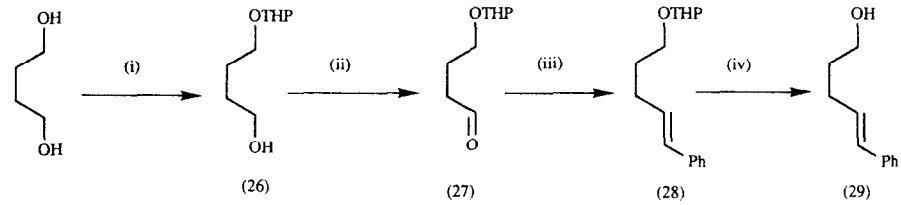
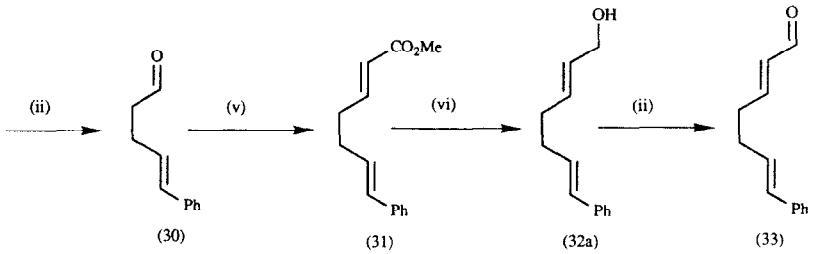
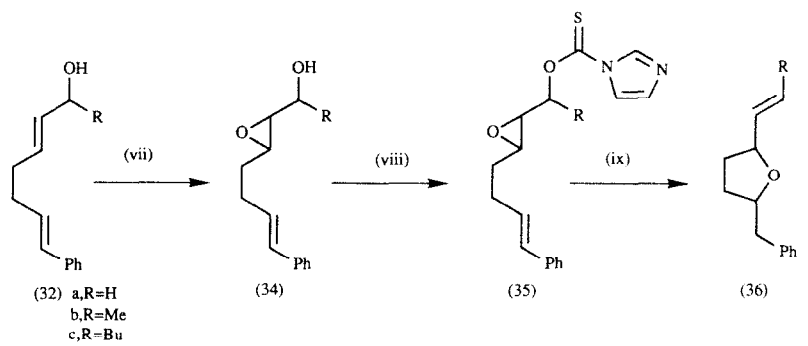
SCHEME 3







REAGENTS: (i) DHP,PPTS,CH_2Cl_2; (ii) PCC,celite,$NaHCO_3$,NaOAc,CH_2Cl_2; (iii) ^{n}BuLi,Diethyl benzyl phosphonate,THF; (iv) "Dowex" 50W-X8(H),MeOH; (v) Trimethyl phosphonoacetate,$K_2CO_3.H_2O$; (vi) DIBAL,Et_2O; (vii) ^{t}Butyl hydroperoxide,$VO(acac)_2$,PhH; (viii) N,N'-thiocarbonyl diimidazole,CH_2Cl_2; (ix) Bu_3SnH,AIBN,THF

TABLE B

STARTING MATERIAL	PRODUCT YIELDS	DIASTEREOMERIC RATIO
(34)	(36)	
a	65%	3:1
b	55%	3:1
c	82%	3:1

EXPERIMENTAL

Infrared spectra were obtained on a Pye-Unicam SP3-100 spectrometer. ^{1}H n.m.r. spectra were recorded at 90 MHz on a Perkin-Elmer R32, at 250 MHz on a Bruker WM250 and at 400 MHz on a Bruker AM400 machine. ^{13}C n.m.r. spectra were recorded at 22.5 MHz on a Jeol FX90Q, at 63 MHz on a Bruker WM250 and at 100 MHz on a Bruker AM400 machine. All n.m.r. experiments were carried out in $CDCl_3$ with TMS as internal reference and chemical shifts are quoted in parts per million (δ p.p.m.). Ultraviolet spectra were recorded on a Philips PU8700 series instrument. Mass spectra were recorded on a VG Micromass 70E or an AEI MS902 instrument.

Where necessary, solvents were distilled before use. Tetrahydrofuran (THF) was distilled from potassium/benzophenone.

3,7-Dimethyl-2,3-epoxy-6-octenol (12a).[5] - tert-Butyl hydroperoxide (4.4 ml, 44 mmol, 80% solution in di-tert-butyl peroxide) was added dropwise over 10 min to a refluxing solution of geraniol (5.0 g, 32 mmol) and vanadium(III) acetylacetonate (20 mg) in benzene (40 ml). After 1 h the reaction mixture was cooled and washed with a saturated aqueous solution of sodium thiosulphate until the washings were colourless. The solution was dried and evaporated to dryness. Chromatography on silica gel with dichloromethane afforded the epoxide (12a) as a colourless oil (5.1 g, 94%); $\bar{\nu}_{max}$ 3440 (OH) and 875 (HC=C) cm^{-1}, δ_H (90 MHz) 1.28 (3H, s, $\underline{H}_3CCO$), 1.48 (2H, m, $C\underline{H}_2CH_2CH=$), 1.60 (3H, s, $C(CH_3)C\underline{H}_3$), 1.67 (3H, s, $C(CH_3)C\underline{H}_3$) 2.08 (2H, m, $C\underline{H}_2CH=$), 2.96 (1H, t, J 5Hz, $C\underline{H}(O)$), 3.43 (1H, bs, $O\underline{H}$), 3.72 (2H, m, $C\underline{H}_2$-OH) and 5.09 (1H, bt, J 7Hz; $C\underline{H}=C(CH_3)_2$); δ_C (23 MHz) 16.4, 17.2, 23.4, 25.3, 38.3, 60.7, 60.8, 63.0, 123.2 and 131.5. m/z 170 ($\underline{M}^+$, 1%), 110 (31) and 109 (100). (Found: $\underline{M}^+$, 170.1321. $C_{10}H_{18}O_2$ requires $\underline{M}$ 170.1307).

Formation of 3,7-Dimethyl-2,3-epoxy-6-octenyl-1-oxythiocarbonylimidazolide (13a) and treatment with $^{n}Bu_3SnH$ and AIBN. - 3,7-Dimethyl-2,3-epoxy-6-octen-1-ol (12a) (0.500 g, 2.9 mmol) and 1,1'-thiocarbonyldiimidazole (1.050 g, 5.9 mmol) were heated under reflux in dry dichloromethane (30 ml) for 1 h. After cooling the solvent was removed in vacuo to afford the imidazolide (13a) as a viscous orange oil. The derivative (13a) was dissolved in dry, degassed THF (50 ml) heated to reflux with $^{n}Bu_3SnH$ (2.3 ml, 8.6 mmol) under nitrogen. A solution of AIBN (20 mg) in THF (2 ml) was added dropwise over 1 h. The mixture was heated under reflux for a further 3 h. On cooling, the solvent was removed by rotary evaporation to afford an orange oil. Chromatography on alumina with hexane resulted in removal of all imidazole and the majority of

the tin residues. Further chromatography on silica gel with dichloromethane afforded tetrahydrofurans (15a) and (16a)[9] as a 3:1 mixture in the form of a colourless oil (63 mg, 14%); $\bar{\nu}_{max}$ 1640 (C=C), 1050 (ether) and 980 ($HC=CH_2$) cm^{-1}; δ_H (400 MHz) 0.86 and 0.87 (3H, 2 x d, J 6.7Hz, $CHCH_3$), 0.95 and 0.99 (3H, 2 x d, J 6.7Hz, $CHCH_3$), 1.30 (3H, s, CCH_3), 1.56-1.75 (3H, m $CH(CH_3)_2$, CH_2CHO), 1.83-1.90 (2H, m, $CH_2C(CH_3)$, 3.68 (1H, m, CHO), 4.97 and 4.98 (1H, 2 x dd, J 10.6 and 1.7Hz. $H\diagdown C=C\diagup H$), 5.17 and 5.21 (1H, 2 x dd J 17.3 and 1.6 Hz, $H\diagdown C=C\diagup H$), 5.88 and 5.92 (1H, 2 x dd, J 10.6 and 17.3 Hz, $CH=CH_2$), δ_C (100 MHz) 18.1, 18.4, 19.2, 19.7, 26.5, 27.1, 28.2, 29.1, 33.0, 33.5, 37.2, 38.2, 82.3,84.2, 84.9, 111.0, 111.2, 144.3 and 145.0; m/z 154 (1%), 139 (17) and 111 (95). (Found: M^+ 154.1395. $C_{10}H_{18}O$ requires M 154.1358).

4,8-Dimethyl-3,7-nonadien-2-ol (11b).[10] - Methyl lithium (23 ml, 1.40 M in diethyl ether, 33 mmol) was added dropwise to a stirring solution of citral (5.0 g, 33 mmol) in dry diethyl ether (100 ml) at -78°C under nitrogen. After stirring for 2 h the resulting yellow solution was warmed up to room temperature and water (5 ml) was added. The pale yellow solution was washed with water (25 ml) and brine (25 ml), dried and evaporated to dryness. Chromatography on silica gel with diethyl ether - hexane (1:3) afforded the alcohol as a colourless oil (3.9 g, 71%); $\bar{\nu}_{max}$ 3340 (OH) 1675 (C=C) and 880 (HC=C) cm^{-1}; δ_H (90 MHz) 1.19 (3H, d, J 6Hz, $C(OH)CH_3$), 1.60 (3H, s, $(CH_2)_2CH(CH_3)=$), 1.67 (6H, s, $(CH_3)_2C=$), 1.90-2.40 (4H, bm, $=CH(CH_2)_2$), 2.63 (1H, bs, OH), 4.51 (1H, m, CH(OH)) and 4.95-5.35 (2H, bm, $(=CH)_2$); δ_C (23 MHz) 16.0, 17.3, 22.9, 23.4, 25.3, 26.3, 26.4, 32.0, 39.3, 63.8, 64.3, 123.9, 129.4, 130.3, 131.1, 131.7, 136.3 and 136.5; m/z 168 (M^+, 1%), 150 (2) and 69 (100). (Found: M^+ 168.1511. $C_{11}H_{20}O$ requires M 168.1514).

4,8-Dimethyl-3,4-epoxy-7-nonen-2-ol (12b). - Tert-Butyl hydroperoxide (1.1 ml, 11 mmol, 80% solution in di-tert-butyl peroxide) was added dropwise over 10 min to a refluxing solution of 2,6-dimethyl-2,6-nonadien-8-ol (11b) (1.3 g, 8 mmol) and vanadium(III) acetylacetonate (20 mg) in benzene (30 ml). After 1 h the reaction mixture was cooled and washed with a saturated aqueous solution of sodium thiosulphate until the washings were colourless. The solution was dried and evaporated to dryness. Chromatography on silica gel with diethyl ether - hexane (1:1) afforded the epoxide (12b) as a colourless oil (1.4 g, 93%); $\bar{\nu}_{max}$ 3 400 (OH), 1 250 (CO, epoxide) and 880 (CH=C) cm^{-1}; δ_H (90 MHz) 1.27 (6H, m, $CH(OH)CH_3$, H_3CCO), 1.61 (3H, s, $=C(CH_3)CH_3$), 1.68 (3H, s, $=C(CH_3)CH_3$), 1.80-2.40 (4H, bm, $=C(CH_2)_2$), 2.71 (1H, d, J 8Hz, CH(O)), 3.21 (1H, bs, OH), 3.64 (1H, m, CH(OH)) and 5.10 (1H, bt, J 7Hz, =CH); δ_C (23 MHz) 16.4, 16.8, 17.5, 19.0, 19.4, 20.8, 22.1, 23.7, 23.9, 25.4, 26.4, 33.1,

38.6, 61.3, 61.9, 65.7, 66.0, 66.3, 66.6, 67.8, 69.1, 123.3, 123.5 and 131.8; m/z 139 ($M^+ - C_2H_5O$, 2%), 75 (4) and 69 (46).

Formation of 4,8-dimethyl-3,4-epoxy-7-nonenyl-2-oxythiocarbonyl imidazolide (13b) and treatment with $^nBu_3SnH$ and AIBN. 2,6-dimethyl-6,7-epoxy-2-nonen-8-ol (12b) (0.500 g, 2.7 mmol) and 1,1'-thiocarbonyldiimidazole (0.980 g, 5.5 mmol) were heated under reflux in dry dichloromethane (30 ml) for 1 h. After cooling the solvent was removed under reduced pressure to afford the imidazolide (13b) as a viscous orange oil. The derivative (13b) was dissolved in dry, degassed THF (50 ml) and was heated to reflux with $^nBu_3SnH$ (2.3 ml, 8.6 mmol) under nitrogen. A solution of AIBN (20 mg) in THF (2 ml) was added dropwise over 1 h. The mixture was heated under reflux for a further 3 h. On cooling the solvent was removed under reduced pressure to afford an orange oil. Chromatography on alumina with hexane removed all the imidazole and the majority of the tin residues. Further chromatography on silica gel G with dichloromethane afforded as colourless oils tetrahydrofurans (15b) and (16b) as a 6:1 mixture (244 mg, 59%) and bicyclic ether (17b) (62 mg, 14%).

Tetrahydrofurans (15b) and (16b): $\bar{\nu}_{max}$ 1 660 (C=C), 1 050 (ether) and 965 (HC=CH) cm^{-1}; δ_H (400 MHz) 0.85 and 0.86 (3H, 2 x d, J 6.7Hz, $CHCH_3$), 0.94 and 0.98 (3H, 2 x d, J 6.7Hz, $CHCH_3$), 1.27 (3H, s, CCH_3), 1.58-1.79 (3H, m, $CH(CH_3)_2$, CH_2CHO), 1.67 (3H, dd, J 6.1 and 1.1Hz, $=CHCH_3$), 1.81-1.88 (2H, m, CH_2 $C(CH_3)$), 3.67 (1H, ddd, J 6.4, 6.4 and 6.4Hz, CHO) and 5.48-5.62 (2H, m, $CH=CHCH_3$); δ_C (23 MHz) 17.6, 18.2, 18.4, 19.2, 19.7, 26.5, 27.4, 28.5, 29.2, 33.2, 33.5, 37.8, 38.6, 81.9 , 84.2, 84.5, 121.8, 137.5 and 138.1; m/z 168 (4%), 125 (54) and 81 (54) (Found: M^+ 168.1529. $C_{11}H_{20}O$ requires M 168.1514).

Bicycle (17b): $\bar{\nu}_{max}$ 1 380 and 1 375 ($C(CH_3)_2$) and 1 150 (ether) cm^{-1}; δ_H (250 MHz) 0.89 (3H, s, $C(CH_3)CH_3$), 0.92 (3H, t, J 7.4Hz, CH_2CH_3). 1.07 (3H, s, $C(CH_3)CH_3$), 1.34 (3H, s, CCH_3). 1.00-1.45 and 1.52-1.85 (7H, m, CH_2CH_2, $CHCH_2CH_3$) and 3.78 (1H, d, J 4.8Hz, CHO); δ_C (23 MHz) 14.3, 19.7, 20.1, 21.7, 26.8, 28.8, 32.7, 41.9, 59.2, 86.3 and 88.2; m/z 168 (8%), 139 (45) and 110 (80). (Found: M^+ 168.1520. $C_{11}H_{20}O$ requires M 168.1514).

7,11-Dimethyl-6,10-dodecadien-5-ol (11c).[10] - n-Butyl lithium (21 ml, 1.55 M in hexanes, 33 mmol) was added dropwise to a stirring solution of citral (5.0 g, 33 mmol) in dry diethyl ether (100 ml) at -78°C under nitrogen. After stirring for 2 h the resulting yellow solution was warmed up to room temperature and water (5 ml) added. The pale yellow solution was washed with water (25 ml) and brine (25 ml), dried and evaporated to dryness. Chromatography on silica gel with diethyl ether - hexane (1:9) afforded the

alcohol (11c) as a colourless oil (5.3 g 76%); $\bar{\nu}_{max}$ 3 320 (OH) and 1 670 (C=C) cm^{-1}; δ_H (90 MHz) 0.90 (3H, bt, J 5Hz, $(CH_2)_3CH_3$), 1.05 (6H, bm, $(CH_2)_3CH_3$), 1.60 (3H, s, $(CH_2)_2$ $CH(CH_3)$=), 1.67 (6H, s, $(CH_3)_2C$=), 2.30 (5H, m, =$CH(CH_2)_2$, OH), 4.34 (1H, m, CH(OH)) and 4.95-5.30 (2H, bm, $(=CH)_2$). δ_C (23 MHz) 13.7, 16.2, 17.2, 22.4, 22.9, 25.2, 26.2, 26.4, 27.4, 27.5, 32.1, 37.2, 39.3, 67.7, 68.1, 123.9, 128.5, 129.3, 130.9, 131.4, 136.9 and 137.3; m/z 210 (M^+, 5%), 192 (13), 69 (100) and 57 (31). (Found: M^+ 210.1978. $C_{14}H_{26}O$ requires M 210.1984).

7,11-Dimethyl-6,7-epoxy-10-dodecen-5-ol (12c). - tert-Butyl hydroperoxide (1.9 ml, 19 mmol, 80% solution in di-tert-butyl peroxide) was added dropwise over 10 min to a refluxing solution of 2,6-dimethyl-2,6-dodecadien-8-ol (11c) (3.0 g, 14 mmol) and vanadium(III) acetylacetonate (20 mg) in benzene (30 ml). After 1 h the reaction mixture was cooled and washed with an aqueous solution of sodium thiosulphate until the washings were colourless. The solution was dried and evaporated to dryness. Chromatography on silica gel with diethyl ether - hexane (1:10) afforded the epoxide (12c) as a colourless oil (2.6 g, 83%); $\bar{\nu}_{max}$ 3 440 (OH) and 1 250 (epoxide); δ_H (250 MHz) 0.92 (3H, t, J 6.8Hz, $(CH_2)_3CH_3$), 1.30 (3H, s, H_3CCO), 1.40-1.80 (6H, bm, $(CH_2)_3CH_3$), 1.61 (3H, s, $=C(CH_3)CH_3$), 1.69 (3H, s, $=C(CH_3)CH_3$, 2.03-2.12 (4H, bm, $=CH(CH_2)_2$), 2.61 (1H, bs, OH), 2.70 and 2.73 (1H, 2 x d, J 2.4Hz, C(O)H), 3.47 (1H, m, CH(OH)) and 5.07 (1H, m, =CH); δ_C (23 MHz) 13.6, 16.9, 17.2, 21.8, 22.4, 23.5, 23.7, 25.3, 26.3, 26.9, 27.1, 29.4, 33.0, 33.3, 33.6, 38.5, 61.4, 61.9, 67.1, 68.4, 69.4, 69.8, 123.4 and 131.4; m/z 226 (1%). 144 (9), 110 (34) and 69 (100). (Found: M^+ 226.1948. $C_{14}H_{26}O_2$ requires M 226.1932).

Formation of 7,11-dimethyl-6,7-epoxy-10-dodecenyl-5-oxythiocarbonyl imidazolide (13c) and treatment with $^nBu_3SnH$ and AIBN. - 2,6-dimethyl-6,7-epoxy-2-dodecen-8-ol (0.500 g, 2.2 mmol) and 1,1'-thiocarbonyldiimidazole (0.784 g, 4.4 mmol) were heated under reflux in dry dichloromethane (30 ml) for 1 h. After cooling the solvent was removed under reduced pressure to afford the imidazolide (13c) as a viscous orange oil. The derivative (13c) was heated in dry THF (50 ml) to reflux with $^nBu_3SnH$ (1.3 ml, 4.8 mmol) under nitrogen. A solution of AIBN (20 mg) in dry THF (2 ml) was added dropwise over 1 h. The mixture was heated under reflux for a further 3 h. On cooling the solvent was removed under reduced pressure to afford an orange oil. Chromatography on alumina with hexane removed all the imidazole and the majority of the tin residues. Further chromatography on silica gel G with dichloromethane afforded as colourless oils tetrahydrofurans (15c) and (16c) as a 8:1 mixture

(293 mg, 63%) and bicyclic ether (17c) (100 mg, 22%). Pure samples of the cis and trans tetrahydrofurans were obtained by chromatography on silica gel with hexane - dichloromethane (1:1).

Trans-tetrahydrofuran (15c): $\bar{\nu}_{max}$ 1 660 (C=C), 1 070 (CO, ether) and 975 (HC=CH) cm^{-1}; δ_H (250 MHz) 0.86 (3H, d, J 6.8Hz, $CHC\underline{H}_3$), 0.89 (3H, t, J 7.0Hz, $CH_2C\underline{H}_3$), 0.94 (3H, d, J 6.7Hz, $CHC\underline{H}_3$), 1.28 (3H, s, $CC\underline{H}_3$), 1.30-1.37 (4H, m, $(C\underline{H}_2)_2CH_3$), 1.59-1.76 (5H, bm, $C\underline{H}_2$-$C\underline{H}_2$, $C\underline{H}(CH_3)_2$), 1.80-2.04 (2H, m, $=CHC\underline{H}_2$), 3.68 (1H, ddd, J 6.7, 6.7 and 6.7Hz), 5.46 (1H, d, J 15.6 Hz, $C\underline{H}$=$CHCH_2$) and 5.57 (1H, dt, J 15.6 and 6.2Hz); δ_C (23 MHz), 14.0, 18.1, 19.2, 22.3, 27.6, 28.4, 31.7, 32.0, 33.2, 37.8, 82.0, 84.1, 127.4 and 136.2; m/z 210 (M^+, 12%), 195 (100), 127 (21) and 111 (34). (Found: M^+ 210.1968. $C_{14}H_{26}O$ requires M 210.1984).

cis-tetrahydrofuran (16c): $\bar{\nu}_{max}$ 1 660 (C=C), 1 050 (CO, ether) and 975 (HC=CH) cm^{-1}; δ_H (250 MHz) 0.85 (3H, d, J 6.7Hz, $CHC\underline{H}_3$) 0.89 (3H, t, J 6.7 Hz, $CH_2C\underline{H}_3$), 0.98 (3H, d, J 6.7Hz, $CHC\underline{H}_3$), 1.28 (3H, s, $CC\underline{H}_3$), 1.21-1.37 (4H, bm, $(CH_2)_2CH_3$), 1.58-1.96 (5H, m, $CH_2C\underline{H}_2$, $C\underline{H}(CH_3)_2$), 1.97-2.05 (2H, m, $=CHC\underline{H}_2$), 3.68 (1H, m, $C\underline{H}O$), 5.50 (1H, d, J 15.6Hz $C\underline{H}$=$CHCH_2$) and 5.61 (1H, dt, J 15.6 and 6.2 Hz, CH=$C\underline{H}CH_2$); δ_C (23 MHz) 14.1, 18.6, 19.8, 22.4, 26.9, 29.3, 31.8, 32.1, 33.6, 38.7, 82.0, 84.6, 127.4 and 136.8; m/z 210 (M^+, 3%), 195 (60), 127 (16) and 111 (35). (Found: M^+ 210.2014. $C_{14}H_{26}O$ requires M 210.1984).

Bicycle (17c): $\bar{\nu}_{max}$ 1 390 and 1 380 ($C(CH_3)_2$) cm^{-1}; δ_H (250 MHz), 0.88 (3H, s, $C(CH_3)C\underline{H}_3$), 0.89 (3H, t, J 6.5Hz, $CH_2C\underline{H}_3$), 1.06 (3H, s, $C(CH_3)C\underline{H}_3$), 1.38 (3H, s, $C(O)C\underline{H}_3$), 1.10-1.35, 1.54-1.82 (13H, bm, $(C\underline{H}_2)_4CH_3$, $C\underline{H}_2C\underline{H}_2$ and $C\underline{H}(CH_2)_4CH_3$) and 3.78 (1H, d, J, 4.9Hz); δ_C (63 MHz) 14.1, 19.8, 21.5, 22.6, 26.8, 27.3, 28.7, 29.4, 32.4, 32.5, 57.1, 86.2 and 88.1; m/z 210 (7%), 139 (38) and 121 (23). (Found: M^+ 210.1995. $C_{14}H_{26}O$ requires 210.1984).

2,6-Dimethyl-8-tetrahydropyranyloxy-2,6-octadien-1-ol (19).[11] - The tetrahydropyranyl ether of geraniol (19.8 g, 0.083 mol), selenium dioxide (4.7 g, 0.042 mol) and pyridine (14 ml, 0.17 mol) were refluxed in ethanol (150 ml) for 3.5 h. The solution was cooled and filtered through a pad of kieselguhr. The filtrate was evaporated to dryness and taken up in diethyl ether (100 ml). The solution was washed with dilute hydrochloric acid (2 x 30 ml, 2M) and then aqueous copper sulphate solution until the pyridine had been removed. The organic layer was dried and evaporated to dryness. Chromatography on silica gel with diethyl ether - hexane (1:2) afforded the alcohol (19) as a colourless oil (6.1 g, 29%); $\bar{\nu}_{max}$ 3 420 (OH), 1 665 (C=C) and 820 (HC=C) cm^{-1}; δ_H (250 MHz) 1.43-2.00 (6H, bm, $(C\underline{H}_2)_3$), 1.63 (3H, s, $=C(C\underline{H}_3)$), 1.65 (3H, s, $=C(C\underline{H}_3)$), 2.00-2.23 (4H, m, $(C\underline{H}_2)_2$), 3.50 (1H, m, $OCHOC\underline{H}(H)$), 3.90 (1H, m,

OCHOCH(H)), 3.95 (2H, s, CH_2OH), 3.99 (1H, dd, J 11.9 and 7.5 Hz, HCHOTHP), 4.22 (1H, dd, J 11.9 and 6.4 Hz HCHOTHP), 4.61 (1H, t, J 4.0 Hz OCHO) and 5.33 (2H, m, $(=CH)_2$); δ_C (23 MHz) 13.6, 16.3, 19.5, 25.5, 25.8, 30.6, 39.1, 62.1, 63.6, 68.6, 97.7, 121.0, 125.3, 135.2 and 139.5. m/z 236 ($M^+ - H_2O$, 2%), 170 (13), 135 (15) and 101 (16).

3,7-Dimethyl-8-tert-butyldimethylsilyloxy-1-tetrahydropyranyloxy-2,6-octadiene (20). - A solution of the alcohol (19) (5.6 g, 22 mmol) in dry dichloromethane (10 ml) was added to a stirring solution of tert-butyldimethylsilyl chloride (36 g, 2.4 mmol) and 1,8-diazabicylo[5.4.0]undec-7-ene (4.1 g, 27 mmol) in dichloromethane (150 ml). The mixture was left stirring at room temperature for 16 h. The solution was evaporated to dryness and the residue was taken up in diethyl ether (100 ml). The ethereal layer was washed with brine (2 x 20 ml), dried and evaporated to dryness. Chromatography on silica gel with diethyl ether - hexane (1:9) afforded the protected diol (20) as a colourless oil (6.1 g, 75%). (Found: C,68.61; H, 10.84. $C_{21}H_{40}O_3$ Si requires C, 68.40%, H, 10.94%); $\bar{\nu}_{max}$ 1 125 (CO ether), 1 080 (CO, ether) and 840 (HC=C) cm^{-1}; δ_H (250 MHz) 0.05 (6H, s, $Si(CH_3)_2$), 0.89 (9H, s, $C(CH_3)_3$), 1.42-2.03 (6H, bm, $(CH_2)_3$), 1.58 (3H, s, $=C(CH_3)$), 1.67 (3H, s, $=C(CH_3)$), 2.00-2.24 (4H, m, $(CH_2)_2$), 3.50 (1H, m, OCHOCH(H)), 3.88 (1H, m, OCHOCH(H)), 3.99 (2H, s, CH_2-OSi), 4.15 (2H, m, CH_2OTHP), 4.62 (1H, t, J 2.9 Hz, O-CH-O) and 5.36 (2H, m, $(=CH)_2$); δ_C (23 MHz) 5.2, 13.4, 16.4, 18.4, 19.6, 25.6, 26.0, 30.8, 39.3, 62.1, 63.6, 68.6, 97.7, 121.0, 124.0, 134.6 and 139.7; m/z 283 ($M^+ - C_5H_8O$, 1%) 135 (16) and 85 (100).

3,7-Dimethyl-8-tert-butyldimethylsilyloxy-2,6-octadien-1-ol (21).[12] The protected diol (20) (6.1 g, 17 mmol) was stirred with magnesium bromide etherate (13.0 g, 50 mmol) in dry diethyl ether (150 ml) for 16 h. Brine was added dropwise with stirring until all the excess magnesium bromide etherate had been dissolved. The organic material was separated and washed with brine (2 x 30 ml). The solution was dried and evaporated to dryness. Chromatography on silica gel with diethyl ether - hexane (1:4) afforded the alcohol (21) as a colourless oil (1.6 g, 33%) (Found: C, 67.57; H, 11.50. $C_{16}H_{32}O_2Si$ requires C, 67.52; H, 11.34%); $\bar{\nu}_{max}$ 3 450 (OH), 1 665 (C=C) and 835 (HC=C); δ_H (250 MHz) 0.05 (6H, s, $Si(CH_3)_2$), 0.90 (9H, s, $C(CH_3)_3$), 1.58 (3H, s, $=C(CH_3)$), 1.66 (3H, s, $=C(CH_3)$), 1.85 (1H, bs, OH), 2.00-2.24 (4H, m, $(CH_2)_2$), 3.99 (2H, s, CH_2OSi), 4.12 (2H, d, J 6.9 Hz, CH_2OH) and 5.37 (2H, m, $(=CH)_2$); δ_C (23 MHz) - 5.2, 13.4, 16.2, 18.4, 26.0, 39.2, 59.2, 68.6, 123.9, 134.7 and 139.0; m/z 209 ($M^+ - C_4H_9$ and H_2O, 13) and 135 (41).

3,7-Dimethyl-2,3-epoxy-8-tert-butyldimethylsilyloxy-6-octen-1-ol (22). - tert- Butyl hydroperoxide (0.70 ml, 7.0 mmol, 80% solution in di-tert-butyl peroxide) was added dropwise over 10 min to a refluxing solution of the allylic alcohol (21) (1.2 g, 4.2 mmol) and vanadium(III) acetylacetonate (20 mg) in benzene (70 ml). After 1 h the reaction mixture was cooled and washed with a saturated aqueous solution of sodium thiosulphate until the washings were colourless. The solution was dried and evaporated to dryness. Chromatography on silica gel with diethyl ether - hexane (1:1) afforded the epoxide (22) (0.8 g, 63%); $\bar{\nu}_{max}$ 3 440 (OH), 1 245 (CO, epoxide) and 840 (HC=C) cm^{-1}; δ_H (250 MHz) 0.04 (6H, s, Si ($C\underline{H}_3$)$_2$), 0.89 (9H, s, C($C\underline{H}_3$)$_3$, 1.28 (3H, s, C(O)$C\underline{H}_3$), 1.50 (1H, m, C$\underline{H}$(H)C(O)), 1.58 (3H, s, CH=C($C\underline{H}_3$)), 1.72 (1H, m, C$\underline{H}$(H)C(O)), 2.12 (2H, q, $\underline{J}$ 7.6 Hz, =CH$C\underline{H}_2$), 2.55 (1H, bs, O$\underline{H}$), 2.95 (1H, dd, $\underline{J}$ 6.3 and 4.8 Hz; C$\underline{H}$CH_2OH), 3.66 (1H, dd, $\underline{J}$ 12 and 6.3 Hz, C$\underline{H}$(H)OH), 3.76 (1H, dd, $\underline{J}$ 12 and 4.8 Hz, C$\underline{H}$(H)OH), 4.00 (2H, s, $C\underline{H}_2$OSi) and 5.34 (1H, m, =C$\underline{H}$); δ_C (23 MHz) 5.2, 13.4, 16.8, 18.4, 23.2, 26.0, 38.3, 61.0, 61.2, 63.1, 68.5, 123.4 and 135.1; m/z 243 (M^+ - C_4H_9,6) 225 (24), 151 (11) and 121 (27).

The formation of 3,7 Dimethyl-2,3-epoxy-8-tert-butyldimethylsilyloxy-6-octenyl-1-oxythiocarbonyl imidazolide (23) and treatment with $^nBu_3SnH$ and AIBN. - The α,β-epoxide (22) (500 mg, 1.7 mmol) and 1,1'-thiocarbonyldiimidazole (356 mg, 2.0 mmol) were heated under reflux in dry dichloromethane (30 ml) for 1 h. After cooling the solvent was removed in vacuo to afford the imidazolide (23) as a viscous orange oil. The derivative was dissolved in dry, degassed THF (50 ml) and heated to reflux with $^nBu_3SnH$ (1.2 ml, 4.5 mmol) under nitrogen. A solution of AIBN (20 mg) in THF (2 ml) was added dropwise over 1 h. The mixture was heated under reflux for a further 3 h. On cooling the solvent was removed in vacuo to afford an orange oil. Initial chromatography on alumina with hexane resulted in removal of all imidazole and the majority of the tin residues. A second columning on silica gel with hexane - dichloromethane (1:1) afforded the tetrahydrofuran (24) as a mixture of four diastereoisomers in the form of a colourless oil (217 mg, 45%); $\bar{\nu}_{max}$ 1 645 (C=C), 1 045 (CO, ether) and 995 (HC=CH_2) $cm.^{-1}$; δ_H (250 MHz) 0.05 (6H, s, Si($C\underline{H}_3$)$_2$), 0.89 (9H, s, C($C\underline{H}_3$)$_3$), 0.87-1.02 (3H, m, CH($C\underline{H}_3$)), 1.29 (3H, s, C(CH=CH_2)$C\underline{H}_3$), 1.65-1.89 (4H, m, ($C\underline{H}_2$)$_2$), 3.47-3.59 (2H, m, $C\underline{H}_2$OTBDMS), 4.97 (1H, dd, $\underline{J}$ 10.6 and 1.6 Hz $^{H}\!\!\searrow\!C{=}C\!\!\nearrow^{H}$), 5.17 and 5.20 (1H, 2 x dd, $\underline{J}$ 17.3 and 1.6 Hz, $^{H}\!\!\searrow\!C{=}C\!\!\nearrow^{H}$) and 5.87 (1H, dd, $\underline{J}$ 17.3 and 10.6 Hz); δ_C (23 MHz) 5.3, 12.7, 12.9, 13.1, 13.3, 18.4, 26.0, 26.4, 26.7, 27.1, 27.3, 28.7, 29.2, 29.4, 29.6, 37.3, 37.4, 38.2, 38.3, 41.0, 41.3, 41.5, 65.7, 65.9, 80.3, 80.4, 80.7, 82.0, 82.2, 111.0, 144.4 and 145.1; m/z 284 (M^+, <1%), 269, (11), 227 (87) and 135 (100) (Found; $\underline{M}^+$ 284.2148. $C_{16}H_{32}O_2Si$ requires $\underline{M}$ 284.2172).

2-(2'-hydroxy-1'-methyl)-ethenyl-5-methyl tetrahydrofuran (18). - Substituted tetrahydrofuran (24) (210 mg, 0.7 mmol) was stirred with tetrabutylammonium fluoride (1.0 ml, 1.0 M solution in THF, 1.0 mmol) in dry THF (3 ml) for 18 h. The solvent was removed by rotary evaporation and the residue was taken up in diethyl ether (20 ml) and was washed with brine (2 x 5 ml). The organic material was dried and evaporated to dryness. The resulting oil was chromatographed on flash silica with diethyl ether - hexane to afford the derived alcohol as a mixture of four diastereoisomers (5:5:2:1 by ^{1}H nmr) in the form of a colourless pungent oil (65 mg, 55%). Further chromatography on silica gel with dichloromethane - diethyl ether - hexane (1:1:2) afforded a pure sample of one of the minor diastereoisomers (lilac alcohol-c) and almost pure samples of the two major diastereoisomers (lilac alcohol-a and -b).

G.c. comparisons and coinjections with authentic lilac alcohols were performed on a Pye Series 104 machine at 140°C using a 1.5 m x 6 mm DEGS column and a helium flow rate of 40 ml/min.

Mixture; $\bar{\nu}_{max}$ 3 420 (OH), 1 645 (C=C) and 1 030 (CO, ether) cm^{-1}; δ_H (250 MHz) 0.79, 0.81, 0.91 and 0.95 (3H, 4 x d, J 7.0 Hz $CHC\underline{H}_3$), 1.32 (3H, s, $C(CH{=}CH_2)C\underline{H}_3$), 1.68-2.07 (4H, m, $(C\underline{H}_2)_2$), 3.04 (1H, bm, O<u>H</u>), 3.57-3.82 and 4.11-4.14 (3H, bm, C<u>H</u>(O) and $C\underline{H}_2OH$), 5.02 (1H, m, $^{H}\!\!>\!C{=}C\!<^{\underline{H}}_{H}$), 5.17, 5.18 and 5.21 (1H, 3 x dd, J 15.8 and 1.5 Hz, $^{H}\!\!>\!C{=}C\!<^{H}_{H}$) and 5.80-5.93 (1H, m, $^{\underline{H}}\!\!>\!C{=}C\!<^{H}_{H}$) δ_C (23 MHz) 12.0, 13.4, 13.6, 14.0, 26.6, 26.7, 26.9, 27.3, 27.6, 30.6, 31.0, 36.5, 37.0, 37.3, 38.5, 41.1, 66.2, 68.4, 68.6, 82.1, 82.8, 83.4, 85.1, 85.4, 111.4, 111.8, 143.6 and 144.3; m/z 170 (M^+, 1%), 155 (13), 143 (2), 111 (100) and 43 (63). (Found: M^+ 170.1318. $C_{10}H_{18}O_2$ requires M 170.1307).

Lilac alcohol-c; δ_H 0.95 (3H, d, J 7.0 Hz, $CHC\underline{H}_3$), 1.30 (3H, s, $C(CH{=}CH_2)C\underline{H}_3$), 1.74-2.01 (4H, bm, $(C\underline{H}_2)_2$), 2.54 (1H, bs, O<u>H</u>) 3.58 (1H, dd, J 10.9 and 4.5 Hz, HC<u>H</u>OH, 3.69 (1H, dd, J 10.9 and 6.5 Hz, HC<u>H</u>OH), 4.14 (1H, m, C<u>H</u>(O)), 4.99 (1H, dd, J 10.7 and 1.3 Hz, $^{H}\!\!>\!C{=}C\!<^{\underline{H}}_{H}$), 5.18 (1H, dd, J 17.3 and 1.3 Hz, $^{H}\!\!>\!C{=}C\!<^{H}_{H}$) and 5.94 (1H, dd, J 17.3 and 10.7 Hz, $^{\underline{H}}\!\!>\!C{=}C\!<^{H}_{H}$); δ_C (100 MHz) 12.3, 25.6, 28.0, 37.7, 38.6, 66.3, 82.0, 82.6, 111.6 and 144.1.

2-(2'-hydroxy-1'-methyl)ethyl-5-ethenyl-5-methyl tetrahydrofuran-tosylate (25). - A sample of alcohol (18) (55 mg, 0.32 mmol) with predominantly trans stereochemistry across the ring (trans:cis, 8:1 by ^{1}H nmr) was stirred with p-toluenesulphonyl chloride (118 mg, 0.62 mmol) in dry pyridine (3 ml) for 16 h. The solution was diluted with diethyl ether (50 ml) and washed with aqueous copper sulphate solution and then with saturated brine. The organic solution was dried and then evaporated to dryness. Chromatography on flash silica with diethyl ether - hexane (1:3) afforded tosylate (25) as predominantly a mixture of two diastereoisomers in the form of a viscous,

colourless oil (80 mg, 77%); (Found: C, 63.02; H, 7.51. $C_{17}H_{24}O_4S$ requires; C, 62.91, H, 7.46%). $\bar{\nu}_{max}$ 1 645 (C=C), 1 375 and 1 185 (OSO_2) cm^{-1}; δ_H (250 MHz) 0.91 and 0.95 (3H, 2 x d, J 7.0 Hz, $CHCH_3$), 1.21 and 1.22 (3H, 2 x s, $C(CH=CH_2)CH_3$), 1.56-1.99 (4H, bm, $(CH_2)_2$), 2.45 (3H, s, CH_3), 3.68-4.22 (3H, m, CH_2-O and CH(O)) 4.95 (1H, dd, J 10.7 and 1.6 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{H}$) 5.08 and 5.10 (1H, 2 x dd, J 17.2 and 1.6 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{H}$), 5.78 and 5.79 (1H, 2 x dd, J 17.3 and 10.7 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{H}$), 7.35 (2H, d, J 8.1 Hz, ArH) and 7.78 (2H, d, J 8.1 Hz ArH); δ_C 12.0, 13.3, 21.6, 26.6, 26.9, 27.2, 28.7, 29.3, 37.0, 37.2, 37.9, 38.9, 39.2, 73.0, 73.2, 78.9, 79.5, 79.9, 82.7, 82.8, 111.3, 128.0, 129.9, 143.8 and 144.7; m/z 324 (M^+, 8%), 155 (31) and 111 (100). (Found M^+ 324.1411. $C_{17}H_{24}SO_4$ requires 324.1395).

2-(1'-methyl)ethyl-5-ethenyl-5-methyl tetrahydrofuran (15a and 16a). - Tosylate (25) (80 mg, 0.25 mmol) was heated under reflux with lithium aluminium hydride (38 mg, 1.0 mmol) in diethyl ether (40 ml) for 8 h. After cooling aqueous diethyl ether was added dropwise until effervescence ceased. Aqueous sodium hydroxide solution (5 ml, 2M) was added with stirring. The white gelatinous precipitate formed was removed by filtration through a pad of Kieselguhr. The ethereal solution was separated out and was washed with dilute hydrochloric acid (2 x 5 ml) and saturated brine (5 ml). The solution was dried and evaporated to dryness in vacuo to afford a yellow oil. Chromatography on flash silica with diethyl ether - hexane (1:4) afforded the tetrahydrofurans (15a and 16a) in 8:1 ratio in the form of a colourless oil (21 mg, 55%) $\bar{\nu}_{max}$ 1 640 (C=C) and 1 050 (CO, ether) cm^{-1}; The lines associated with the major isomer are the following: δ_H (400 MHz) 0.87 (3H, d, J 6.8 Hz, $CHCH_3$), 0.95 (3H, d, J 6.7 Hz, $CHCH_3$), 1.30 (3H, s, CCH_3, 1.59-1.75 (3H, bm, $CH(CH_3)_2$, CH_2CHO), 1.82-1.90 (2H, bm, $CH_2C(CH_3)$), 3.68 (1H, m, CHO), 4.98 (1H, dd, J 10.6 and 1.7 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{H}$), 5.17 (1H, dd, J 17.3 and 1.7 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{H}$) and 5.88 (1H, dd, J 10.6 and 17.3 Hz, $^{H}\!>\!C\!=\!C\!<^{H}_{H}$); δ_C (100 MHz) 18.0, 19.2, 27.1, 28.2,. 33.0., 37.2, 82.3, 84.3, 111.0 and 144.2.

4-Tetrahydropyranyloxy-butan-1-ol (26)[9]. - Butane-1,4-diol (10.0 g, 0.11 mol), dihydropyran (9.71 g of 97% material, 0.11 mol) and pyridinium para-toluene sulphonate (2.80 g, 0.011 mol) were mixed in dry, distilled dichloromethane (100 ml) and the mixture was stirred for 18 h. After diluting with diethyl ether (50 ml) and washing with half-saturated brine (50 ml) the solution was dried ($MgSO_4$) and solvent evaporation in vacuo afforded a yellow liquid (17.0 g). Chromatography on silica gel with diethyl ether - hexane (1:1) separated the title compound (26) as a colourless oil (8.92 g, 46%). (Found: C, 61.84; H, 10.66. $C_9H_{18}O_3$ requires C, 62.04; H, 10.41%); $\bar{\nu}_{max}$

(film) 3420, 2960, 2880, 1450, 1360, 1130, 1030 and 875 cm^{-1}; δ_H (90 MHz; $CDCl_3$), 1.40-1.90 (10H, m, 5 x C-C<u>H</u>$_2$-C), 3.35-4.05 (6H, m, 3 x C-C<u>H</u>$_2$-O) and 4.65 (1H, m, O-C<u>H</u>(CH_2R)-O); δ_C (22.5 MHz; $CDCl_3$) 19.3, 25.3, 26.2, 29.6, 30.4, 62.0, 67.2 and 98.6; <u>m/z</u> (f.a.b., + ve ion; MNBA) 175 (<u>M</u>H^+, 9%) and 85 (100).

4-<u>Tetrahydropyranyloxy-butanal</u> (27)[9]. - 4-Tetrahydropyranyloxy-butan-1-ol (26) (990 mg, 5.69 mmol), pyridinium chlorochromate (7.53 g, 34.9 mmol), celite (7.7 g), sodium acetate (480 mg, 5.85 mmol) and sodium bicarbonate (490 mg, 5.83 mmol) were dispersed in dry, distilled dichloromethane (50 ml) and the mixture was stirred at room temperature for 2 h. Diethyl ether (50 ml) was added and the mixture was filtered through a pad of silica gel. Evaporation of solvent <u>in vacuo</u> afforded an orange oil which was purified by chromatography on silica gel with diethyl ether - hexane (1:1) to yield the title compound (27) as a colourless oil (888 mg, 91%); $\bar{\nu}_{max}$ (film) 2940, 2870, 2720, 1720, 1440, 1145 and 1120 cm^{-1}; δ_H (90 MHz; $CDCl_3$), 1.45-2.10 (8H, m, 4 x C-C<u>H</u>$_2$-C), 2.55 (2H, td, <u>J</u> 8, 1Hz, C<u>H</u>$_2$C(O)H), 3.30-4.00 (4H, m, 2 x C-C<u>H</u>$_2$-O), 4.60 (1H, m, O-C<u>H</u>(CH_2R)-O) and 9.90 (1H, t, <u>J</u> 1 Hz, -C(O)<u>H</u>); δ_C (22.5 MHz; $CDCl_3$) 18.9, 22.2, 25.0, 30.1, 40.5, 61.5, 65.9, 98.2 and 202.5; <u>m/z</u> (f.a.b., +ve ion; MNBA) 173 (<u>M</u>H^+, 1%) and 85 (100); <u>m/z</u> (100°C) 87.0419 (100%) (<u>M</u>-THP requires 87.0446).

5-<u>Phenyl</u>-1-<u>tetrahydropyranyloxy-pent-4-ene</u> (28). - Diethyl benzyl phosphonate (9.64g, 42.2 mmol) was dissolved in dry, deoxygenated THF (100 ml) and ^{n}butyllithium (28.2 ml of 1.50 M soln. in hexanes, 42.3 mmol) was added dropwise, with stirring, under nitrogen, at -78°C. After stirring for a further 1.5 h, 4-tetrahydropyranyloxy-butanal (27) (6.06 g, 35.2 mmol) in THF (10 ml) was added dropwise. The mixture was warmed to room temperature and stirring was continued for a further 16 h. Solvent was removed <u>in vacuo</u> and the residue was taken up in diethyl ether (50 ml) and water (50 ml). The organic phase was separated, washed with saturated brine (50 ml), dried (Na_2SO_4) and solvent removal <u>in vacuo</u> afforded a yellow liquid (10.6 g). Chromatography on silica gel with chloroform-hexane (1:1) yielded the purified <u>title compound</u> (28) as a colourless oil (3.97 g, 46%); $\bar{\nu}_{max}$ (film) 3080, 3050, 3020, 2940, 2870, 1595, 1495, 1440, 1035, 745 and 695 cm^{-1}; λ_{max} (EtOH) 251.1 nm (19,600), 284.7 (1200) and 293.6 (680); δ_H (250 MHz; $CDCl_3$) 1.49-1.89 (8H, m, 4 x C-C<u>H</u>$_2$-C), 2.31 (2H, dt, <u>J</u> 7.1, 7.1 Hz, CH_2C<u>H</u>$_2$CH=), 3.47 (2H, m, -C<u>H</u>$_2$O), 3.84 (2H, m, -C<u>H</u>$_2$O), 4.59 (1H, t, <u>J</u> 3.5Hz, O-C<u>H</u>(CH_2R)-O), 6.24 (1H, dt, <u>J</u> 15.8, 6.6 Hz, -CH_2C(<u>H</u>)=C(H)Ph (<u>trans</u>)), 6.41 (1H, d, <u>J</u> 15.8 Hz, -CH_2C(H)=C(<u>H</u>)Ph (<u>trans</u>)) and 7.15-7.36 (5H, m, ArH); δ_C (22.5 MHz; $CDCl_3$) 19.4, 25.4, 29.3, 29.5, 30.6, 61.8, 66.6, 98.5, 125.7,

126.6, 128.1, 130.0 and 137.6; m/z (140°C) 246 (M^+, 1%), 162 (20) and 85 (100). (Found: M^+, 246.1619, $C_{16}H_{22}O_2$ requires M, 246.1620).

5-Phenyl-pent-4-en-1-ol (29)[10]. - 5-Phenyl-1-tetrahydropyranyloxy-pent-4-ene (28) (2.28 g, 9.27 mmol) and "Dowex" 50W-X8(H) (1.51 g) were stirred together in methanol (50 ml) at 45°C for 27 h. The resin was removed by filtration, washed well with methanol, and the solvent was removed in vacuo to yield a colourless liquid (1.8 g). Chromatography on silica gel with chloroform afforded the title compound (29) as a colourless oil (1.26 g, 84%). (Found: C, 81.29; H, 8.99. $C_{11}H_{14}O$ requires C, 81.44; H, 8.69%); $\bar{\nu}_{max}$ (film) 3340, 3080, 3050, 3020, 2930, 2870, 1595, 1495, 1445, 1060, 965, 750 and 700 cm^{-1}; λ_{max} ($CHCl_3$) 254.1 nm (17,300), 284.3 (1,500) and 294.0 (830); δ_H (250 MHz; $CDCl_3$) 1.53 (1H, bs, -OH), 1.70 (2H, tt, J 6.8 Hz, $-CH_2CH_2CH_2-$), 2.31 (2H, dtd, J 7.2, 7.2, 1.2 Hz, $-CH_2CH_2C(H)=C(H)Ph$), 3.69 (2H, t, J 6.4 Hz, $-CH_2CH_2OH$), 6.23 (1H, dt, J 15.8, 6.7 Hz, $-CH_2C(H)=C(H)Ph$ (trans)), 6.42 (1H, d, J 15.8 Hz, $-CH_2C(H)=C(H)Ph$ (trans)) and 7.16-7.37 (5H, m, ArH); δ_C (22.5 MHz; $CDCl_3$) 29.1, 32.1, 61.8, 125.8, 126.7, 128.3, 130.0, 130.2 and 137.6; m/z (120°C) 162 (M^+, 38%), 144 (23), 129 (100), 117 (80) and 91 (75). (Found: M^+, 162.1028, $C_{11}H_{14}O$ requires M, 162.1045).

5-Phenyl-pent-4-enal (30)[11]. - 5-Phenyl-pent-4-en-1-ol (29) (245 mg, 1.51 mmol), pyridinium chlorochromate (0.97 g, 4.50 mmol), celite (0.98 g), sodium acetate (123 mg, 1.50 mmol) and sodium bicarbonate (126 mg, 1.50 mmol) were dispersed in dry, distilled dichloromethane (30 ml) and the mixture was stirred at room temperature for 1 h. Diethyl ether (50 ml) was added and the mixture was filtered through a pad of silica gel. Evaporation of solvent in vacuo afforded an orange oil which was purified by chromatography on silica gel with diethyl ether-hexane (1:1) to give the title compound (30) as a colourless oil (192 mg, 79%); $\bar{\nu}_{max}$ (film) 3080, 3050, 3020, 2920, 2830, 2730, 1720, 1600, 1495, 1450, 970, 755 and 700 cm^{-1}; λ_{max} (EtOH) 251.6 nm (ε 21,500), 283.4 (1,600) and 292.7 (950); δ_H (90 MHz; $CDCl_3$) 2.55 (4H, m, $-CH_2-CH_2-$), 6.05-6.55 (2H, m, $-CH_2C(H)=C(H)Ph$), 7.25-7.50 (5H, m, ArH) and 9.85 (1H, m, -C(O)H); δ_C (22.5 MHz; $CDCl_3$) 25.4, 43.2, 126.0, 127.2, 128.2, 128.5, 131.1, 137.2 and 201.4; m/z (100°C) 160 (M^+, 57%), 132 (13), 117 (43) and 104 (100). (Found: M^+, 160.0893. $C_{11}H_{12}O$ requires M 160.0888).

Methyl 7-phenyl-hepta-2,6-dienoate (31). - 5-Phenyl-pent-4-enal (30) (696 mg, 4.35 mmol), trimethylphosphonoacetate (1.21 g, 6.64 mmol), potassium carbonate (1.22 g, 8.83 mmol) and water (1.0 ml) were stirred together at room temperature for 48 h. Water (30 ml) was added and the product was

extracted with hexane (3 x 30 ml). Drying (Na_2SO_4) and solvent removal *in vacuo* afforded a colourless oil. Chromatography on silica gel with chloroform- hexane (2:3) afforded the *title compound* (31) as a colourless oil (888 mg, 94%); $\bar{\nu}_{max}$ (film) 3080, 3060, 3020, 2950, 2840, 1725, 1660, 1595, 1490, 1435, 970, 745 and 695 cm^{-1}; λ_{max} (EtOH) 251.9 nm (ε 25,300), 283.9 (2,050) and 292.9 (1,220); δ_H (250 MHz; $CDCl_3$) 2.38 (4H, m, $-CH_2CH_2-$), 3.72 (3H, s, $-OCH_3$), 5.87 (1H, d, *J* 15.6 Hz, $-C(H)=C(H)CO_2Me$), 6.18 (1H, m, $-CH_2-C(H)=C(H)Ph$), 6.42 (1H, d, *J* 15.8 Hz, $-C(H)=C(H)Ph$), 7.01 (1H, m, $-CH_2-C(H)=C(H)CO_2Me$) and 7.19-7.36 (5H, m, ArH); δ_C (22.5 MHz; $CDCl_3$) 31.2, 31.8, 51.1, 121.4, 125.9, 126.9, 128.3, 128.6, 130.9, 137.3, 148.1 and 166.6; *m/z* (120°C) 216 (M^+, 29%), 117 (100) and 91 (33). (Found: M^+, 216.1146. $C_{14}H_{16}O_2$ requires *M* 216.1150).

7-*Phenyl*-*hepta*-2,6-*dien* *1-ol* (32a). - Methyl 7-phenyl-hept-2,6-dienoate (31) (856 mg, 3.96 mmol) was dissolved in sodium-dried diethyl ether (25 ml) and to the stirred solution, under nitrogen, at -78°C, diisobutylaluminium hydride (8.75 ml of 1.0 M soln in hexane, 8.75 mmol) was added dropwise. The mixture was stirred at -78°C for 2 h then at room temperature for a further 1 h. Diethyl ether (25 ml) was added and the mixture was washed with sodium hydroxide soln (50 ml, 2% aqueous), water (25 ml), saturated brine (25 ml) and after drying (Na_2SO_4), solvent evaporation *in vacuo* afforded a colourless oil. Chromatography on silica gel with diethyl ether-hexane (1:1) yielded the *title compound* (32a) as a colourless oil (699 mg, 94%); $\bar{\nu}_{max}$ (film) 3340, 3080, 3060, 3020, 2920, 2850, 1665, 1645, 1595, 1490, 1440, 965, 745 and 690 cm^{-1}; λ_{max} (EtOH), 251.5 nm (ε 17,100), 283.6 (1,310) and 293.3 (850); δ_H (250 MHz; $CDCl_3$) 2.20-2.35 (4H, m, $-CH_2-CH_2-$), 4.10 (2H, d, *J* 4.5 Hz, $=C(H)-CH_2OH$), 5.72 (2H, m, $-CH_2-CH=CH-CH_2-$), 6.21 (1H, dt, *J* 15.8, 6.4 Hz, $-CH_2-C(H)=C(H)Ph$), 6.40 (1H, d, *J* 15.9 Hz, $CH_2-C(H)=C(H)Ph$) and 7.17-7.36 (5H, m, ArH); δ_C (22.5 MHz; $CDCl_3$), 32.0, 32.6, 63.4, 126.0, 126.9, 128.5, 129.7, 129.9, 130.4, 131.9 and 137.7; *m/z* (100°C) 188 (M^+, 23%), 129 (31), 118 (45), 117 (100), 115 (67) and 91 (55). (Found: M^+, 188.1196, $C_{13}H_{16}O$ requires *M*, 188.1201).

2,3-*Epoxy*-7-*phenyl*-*hept*-6-*en*-1-*ol* (34a). - 7-Phenyl-hepta-2,6-dien-1-ol (32a) (150 mg, 0.798 mmol) was dissolved in sodium-dried benzene (25 ml) and vanadyl acetyl acetonate (22 mg) was added. To the stirred solution, at reflux temperature, under nitrogen, *tert*-butylhydroperoxide (120 µl of 80% soln in di-*tert*-butyl peroxide, 0.955 mmol) was added dropwise and the resulting mixture was refluxed for 1 h. After cooling, the solution was washed with saturated aqueous sodium thiosulphate (3 x 20 ml), dried (Na_2SO_4)

and evaporation of solvent *in vacuo* afforded an orange oil. Chromatography on silica gel with diethyl ether-hexane (1:1) yielded the *title compound* (34a) as a colourless oil (118 mg, 72%); $\bar{\nu}_{max}$ (film) 3420, 3020, 2920, 2850, 1595, 1490, 1440, 965, 755 and 695 cm^{-1}; λ_{max} (EtOH) 251.5 nm (ε 13,200), 283.6 (1,090) and 292.5 (710); δ_H (250 MHz; $CDCl_3$) 1.74 (2H, m, $-C\underline{H}_2-C-O$), 2.29-2.42 (3H, m, $-C\underline{H}_2-C=$ and $-O\underline{H}$), 2.95 (1H, td, *J* 4.6, 2.4 Hz, $-CH_2-C\underline{H}-O$ [epoxide]), 3.02 (1H, td, *J* 5.7, 2.2 Hz, $-CH_2-C\underline{H}-O$[epoxide]), 3.58 (1H, dd, *J* 12.7, 4.3 Hz, $-C(H)\underline{H}-OH$), 3.89 (1H, dd, *J* 12.6, 2.1 Hz, $-C(\underline{H})H-OH$), 6.21 (1H, dt, *J* 15.8, 6.8 Hz, $-CH_2C(\underline{H})=C(H)Ph$), 6.43 (1H, d, *J* 15.8 Hz, $-CH_2-C(H)=C(\underline{H})Ph$) and 7.17-7.36 (5H, m, Ar*H*); δ_C (22.5 MHz; $CDCl_3$) 29.3, 31.4, 55.5, 58.7, 61.8, 126.0, 127.0, 128.5, 129.2, 130.8 and 137.5; *m/z* (150°C) 186 ($\underline{M}^+-H_2O$, 7%), 160 (29), 130 (44), 129 (39), 117 (100), 115 (63), 104 (63) and 91 (76). (Found: $\underline{M}^+$, 186.1050. $C_{13}H_{16}O_2-H_2O$ requires *M*, 186.1045).

7-*Phenyl*-*hepta*-2,6-*dienal* (33). - 1-Phenyl-hept-1,5-dien-7-ol (32a) (100 mg, 0.532 mmol), pyridinium chlorochromate (355 mg, 1.65 mmol), sodium acetate (44 mg, 0.54 mmol), sodium bicarbonate (45 mg, 0.54 mmol) and celite (360 mg) were dispersed in dichloromethane (10 ml) and the mixture was stirred at room temperature for 1 h. After diluting with diethyl ether (20 ml) the mixture was filtered through a pad of silica. Solvent removal *in vacuo* afforded a liquid which was purified by chromatography on silica gel with diethyl ether-hexane (1:2) to yield the *title compound* (33) as a colourless oil (75 mg, 75%); $\bar{\nu}_{max}$ (film) 3080, 3060, 3020, 2920, 2850, 2820, 2740, 1690, 1630, 1600, 1500, 1450, 970, 750 and 700 cm^{-1}; λ_{max} (EtOH) 251.5 nm (ε 17,900), 282.8 (1,630) and 292.5 (920); δ_H (250 MHz; $CDCl_3$), 2.39-2.56 (4H, m, $-C\underline{H}_2C\underline{H}_2-$), 6.17 (2H, m, $=C(\underline{H})CHO$ and $-CH_2C(\underline{H})=$), 6.44 (1H, d, *J* 15.8 Hz, $-CH_2C(H)=C(\underline{H})Ph$), 6.87 (1H, dt, *J* 15.6, 6.2 Hz, $-CH_2C(\underline{H})=C(H)CHO$), 7.18-7.36 (5H, m, Ar*H*) and 9.51 (1H, d, *J* 7.9 Hz, $=CH-C(O)\underline{H}$); δ_C (22.5 MHz; $CDCl_3$) 31.2, 32.4, 126.1, 127.3, 128.3, 128.6, 131.4, 133.4, 137.3, 157.1 and 193.7; *m/z* (150°C), 186 ($\underline{M}^+$, 13%), 157 (3), 117 (100), 115 (59) and 91 (37). (Found: $\underline{M}^+$, 186.1035. $C_{13}H_{14}O$ requires *M*, 186.1045).

8-*Phenyl*-*octa*-3,7-*dien*-2-*ol* (32b). - 7-Phenyl-hept-2,6-dienal (33) (150 mg, 0.806 mmol) was dissolved in sodium-dried diethyl ether (25 ml) and to the stirred solution, under argon, at -78°C, methyllithium (as a complex with LiBr, 650 µl of 1.5 M soln in diethyl ether, 0.975 mmol) was added dropwise. The mixture was stirred for 1.5 h at -78°C then for 1.5 h at room temperature. After washing with water (2 x 10 ml) and saturated brine (10 ml) the organic phase was dried (Na_2SO_4). Solvent evaporation *in vacuo* afforded a yellow oil. Chromatography on silica gel with diethyl ether-hexane

(1:1) yielded the title compound (32b) as a colourless oil (162 mg, 99%); $\bar{\nu}_{max}$ (film) 3350, 3080, 3060, 3020, 2970, 2920, 2850, 1600, 1490, 1450, 1060, 965, 745 and 695 cm^{-1}; λ_{max} (EtOH) 252.2 nm (ε 15,400), 283.6 (1,210) and 292.5 (750); δ_H (250 MHz; $CDCl_3$) 1.26 (3H, d, J 6.4 Hz, -CH(OH)C<u>H</u>$_3$), 1.52 (1H, br, -O<u>H</u>), 2.16-2.34 (4H, m, -C<u>H</u>$_2$C<u>H</u>$_2$-), 4.27 (1H, dq, J 6.2, 6.2 Hz, =CH-C<u>H</u>(OH)Me), 5.52-5.74 (2H, m, -CH_2-C(<u>H</u>)=C(<u>H</u>)-CH(OH)Me), 6.21 (1H, dt, J 15.8, 6.1 Hz, -CH_2C(<u>H</u>)=C(H)Ph), 6.39 (1H, d, J 15.9 Hz, -CH_2C(H)=C(<u>H</u>)Ph) and 7.16-7.36 (5H, m, Ar<u>H</u>); δ_C (22.5 MHz; $CDCl_3$) 23.4, 31.8, 32.6, 68.5, 125.9, 126.8, 128.4, 129.5, 129.9, 130.3, 135.0 and 137.7; m/z (150°C) 202 (M^+, 15%), 184 (11), 117 (100) and 91 (53). (Found: M^+, 202.1346. $C_{14}H_{18}O$ requires M, 202.1358).

3,4-Epoxy-8-phenyl-oct-7-en-2-ol (34b). - 8-Phenyl-octa-3,7-dien-2-ol (32b) (140 mg, 0.693 mmol) was dissolved in sodium-dried benzene (20 ml) and the mixture was brought to reflux temperature, with stirring, under nitrogen. Vanadyl acetylacetonate (20 mg) was added, followed by tert-butyl hydroperoxide (110 µl of 80% soln. in di-tert-butylperoxide, 0.875 mmol) dropwise. After refluxing for 1.5 h, the mixture was diluted with diethyl ether (20 ml) and washed with saturated aqueous sodium thiosulphate (3 x 10 ml), dried (Na_2SO_4) and solvent evaporation in vacuo afforded an orange oil. Chromatography on silica gel with diethyl ether-hexane (1:1) yielded the title compound (34b) as a diastereomeric mixture as a colourless oil (104 mg, 69%); $\bar{\nu}_{max}$ (film) 3400, 3080, 3050, 3020, 2970, 2920, 1590, 1490, 1450, 1370, 1075, 970, 750 and 700 cm^{-1}; λ_{max} (EtOH) 251.1 nm (ε 19,500), 283.2 (1,480) and 292.5 (930); δ_H (250 MHz; $CDCl_3$) 1.26 (3H, m, -CH(OH)C<u>H</u>$_3$), 1.58 (1H, s [removed by D_2O shake], -O<u>H</u>), 1.79 (2H, m, -C<u>H</u>$_2$-C-O), 2.37 (2H, m, =CH-C<u>H</u>$_2$), 2.75-3.09 (2H, m, 2 x -C<u>H</u>-O [epoxide]), 3.63 and 3.95 (1H, m, -C<u>H</u>(OH)Me), 6.22 (1H, dt, J 15.8, 6.8 Hz, -CH_2-C(<u>H</u>)=C(H)Ph), 6.44 (1H, d, J 15.9 Hz, -CH_2C(H)=C(<u>H</u>)Ph) and 7.20-7.36 (5H, m, Ar<u>H</u>); δ_C (22.5 MHz; $CDCl_3$) 18.9, 19.8, 26.6, 29.5, 31.4, 54.7, 56.3, 61.9, 62.8, 65.1, 67.7, 126.0, 127.1, 128.5, 129.3, 130.8 and 137.5; m/z (150°C) 218 (M^+, 2%), 200 (3), 130 (76), 117 (100), 115 (64) and 91 (78). (Found: M^+, 218.1322. $C_{14}H_{18}O_2$ requires M, 218.1307).

11-Phenyl-undeca-6,10-dien-5-ol (32c). - 7-Phenyl-hepta-2,6-dienal (33) (73 mg, 0.39 mmol) was dissolved in sodium-dried diethyl ether (10 ml) and to the stirred solution, at -78°C, under nitrogen, n-butyllithium (300 µl of 1.50 M soln. in hexanes, 0.45 mmol) was added dropwise. The mixture was stirred at -78°C for 0.5 h then at room temperature for 1.5 h, diluted with diethyl ether (30 ml), washed with water (2 x 20 ml), saturated brine (20 ml) and

dried (Na_2SO_4). Solvent removal in vacuo afforded the title compound (32c) as a colourless oil (95 mg, 100%); $\bar{\nu}_{max}$ (film) 3350, 3080, 3060, 3030, 2960, 2930, 2860, 1600, 1490, 970, 750 and 700 cm^{-1}; λ_{max} (EtOH) 252.2 nm (ε 18,600), 284.3 (1,500) and 293.3 (930); δ_H (250 MHz; $CDCl_3$) 0.88 (3H, t, J 6.5 Hz, $-CH_2CH_3$), 1.25-1.59 (6H, m, $-CH_2CH_2CH_2-$), 2.18-2.36 (4H, m, CH_2-CH_2) 4.05 (1H, dt, J 6.5 Hz, $=C(H)-CH(OH)-CH_2-$), 5.51 (1H, dd, J 15.4 Hz, 6.9 Hz, $-C(H)=C(H)-CH(OH)-$) 5.68 (1H, dt, J 15.4, 6.3 Hz, $-CH_2-C(H)=C(H)-$) 6.21 (1H, dt, J 15.8, 5.9 Hz, $-CH_2-C(H)=C(H)Ph$), 6.39 (1H, d, J 15.9 Hz, $-C(H)=C(H)Ph$) and 7.16-7.36 (5H, m, ArH); δ_C (22.5 MHz; $CDCl_3$) 14.0, 22.6, 27.6, 32.0, 32.6, 37.1, 72.9, 126.0, 126.9, 128.5, 129.9, 130.4, 130.6, 134.0 and 137.8; m/z (175°C) 244 (M^+, 1%), 169 (3), 117 (100), 115 (18) and 67 (20). (Found: M^+, 244.1804. $C_{17}H_{24}O$ requires M, 244.1827).

6,7-Epoxy-11-phenyl-undec-10-en-5-ol (34c). - 11-Phenyl-undeca-6,10-dien-5-ol (32c) (95 mg, 0.39 mmol) and vanadyl acetyl acetonate (25 mg) were dissolved in sodium-dried benzene (10 ml) and to the stirred, refluxing solution under nitrogen, tert-butyl hydroperoxide (80 µl of 80% soln. in di-tert-butylperoxide, 0.64 mmol) was added dropwise. The mixture was refluxed for 1 h, diluted with diethyl ether (20 ml), washed with saturated aqueous sodium thiosulphate (3 x 15 ml) and dried (Na_2SO_4). Solvent removal in vacuo afforded a green oil which was chromatographed on silica gel with diethyl ether-hexane (1:1) to yield the title compound (34c) as a diastereomeric mixture as a colourless oil (72 mg, 72%); $\bar{\nu}_{max}$ (film) 3450, 3090, 3070, 3040, 2960, 2940, 2870, 1600, 1490, 970, 750 and 700 cm^{-1}; λ_{max} (EtOH) 251.1 nm (28,900), 283.9 (2,730) and 292.9 (1,880); δ_H (250 MHz; $CDCl_3$) 0.89 (3H, t, J 6.3 Hz, CH_2CH_3), 1.24-1.94 (9H, m, 4 x CH_2 + -OH [removed by D_2O shake]), 2.37 (2H, m, $=CH-CH_2-CH_2-$), 2.76-3.10 (2H, m, 2 x -CH-O [epoxide]), 3.44 and 3.79 (1H, m, $-CH(OH)$), 6.23 (1H, dt, J 15.9, 6.7 Hz, $-CH_2C(H)=C(H)Ph$), 6.44 (1H, d, J 15.8 Hz, $-C(H)=C(H)Ph$) and 7.17-7.36 (5H, m, ArH); δ_C (22.5 MHz, $CDCl_3$) 13.9, 22.7, 27.5, 29.4, 31.5, 33.4, 34.1, 54.6, 56.4, 61.2, 62.0, 68.8, 71.5, 126.0, 127.0, 128.5, 129.2, 130.8 and 137.5; m/z (100°C) 260 (M^+, 4%), 160 (12), 144 (22), 130 (100), 117 (85) and 91 (60). (Found: M^+, 260.1765. $C_{17}H_{24}O_2$ requires M, 260.1776).

Formation of 2,3-epoxy-7-phenyl-hept-6-enyl-1-oxythiocarbonyl imidazolide (35a) and treatment with $^nBu_3SnH$-AIBN. - 2,3-Epoxy-7-phenyl-hept-6-en-1-ol (88 mg, 0.43 mmol) was dissolved in dry, distilled dichloromethane (30 ml). N, N'-thiocarbonyldiimidazole (170 mg of 90% material, 0.86 mmol) was added and the mixture was heated under reflux, with stirring for 1 h. After cooling, solvent removal in vacuo afforded the imidazolide (35a) as an orange oil.

This was taken up in dry, deoxygenated THF (80 ml) and the solution was brought to reflux temperature, under nitrogen, with stirring. Tri-n-butyltin hydride (280 μl, 1.04 mmol) was added in one portion, followed by AIBN (5 mg) in THF (2 ml) over a 0.5 h period. The mixture was refluxed for 16 h and solvent removal in vacuo afforded an orange oil. Chromatography on alumina with hexane then on silica with hexane-dichloromethane (1:1) yielded 2-benzyl- 5-ethenyl tetrahydrofuran (36a) as a 3:1 diastereomeric mixture. Products were isolated as colourless liquids (total yield 52 mg, 65%).

2-Benzyl-5-ethenyl tetrahydrofuran (36a); $\bar{\nu}_{max}$ (film) 3090, 3070, 3040, 2980, 2940, 2870, 1645, 1600, 1495, 1455, 1055, 750 and 705 cm^{-1}; δ_H (400 MHz; $CDCl_3$) 1.63 (2H, m, $-CH(O)-C\underline{H}_2-CH_2$), 1.98 (2H, m, $-CH(O)-C\underline{H}_2-CH_2$), 2.74 (1H, dd, J 13.5, 7.2 Hz, $-HC\underline{H}Ph$), 3.00 (1H, dd, J 13.5, 5.5 Hz, $-\underline{H}CHPh$), 4.12-4.46 (2H, m, $C\underline{H}-O-C\underline{H}$), 5.09 (1H, dm, J 10.3 Hz, $-HC=C(H)\underline{H}$), 5.24 (1H, dm, J 17.1 Hz, $-HC=C(\underline{H})H$), 5.85 (1H, m, $CH-C\underline{H}=CH_2$) and 7.18-7.30 (5H, m, Ar$\underline{H}$); δ_C (22.5 MHz; $CDCl_3$) 30.6, 31.3, 31.7, 32.3, 42.2, 42.4, 79.8, 80.2, 80.4, 114.6, 114.9, 126.1, 128.2, 129.3, 138.8 and 139.6; m/z (180°C) 188 (M^+, 14%), 97 (97), 91 (100), 79 (45) and 69 (45). (Found: M^+, 188.1240. $C_{13}H_{16}O$ requires M, 188.1201).

Formation of 3,4-epoxy-8-phenyl-oct-7-enyl-2-oxythiocarbonyl imidazolide (35b) and treatment with $^nBu_3SnH$-AIBN. - 3,4-Epoxy-8-phenyl-oct-7-en-2-ol (34b) (99 mg, 0.45 mmol) was dissolved in dry, distilled dichloromethane. N, N'-thiocarbonyl diimidazole (170 mg, 0.95 mmol) was added and the mixture was refluxed under nitrogen for 1 h. After cooling, solvent evaporation in vacuo afforded the imidazolide (35b) as an orange solid. This was taken up in dry, deoxygenated THF (50 ml) and the solution was brought to reflux, with stirring, under nitrogen. A solution of tri-n-butyltin hydride (260 μl, 0.97 mmol) and AIBN (10 mg) in THF (1 ml) was added over a period of 1 h, and refluxing was continued for a further 18 h. After cooling, evaporation of solvent in vacuo afforded a dark orange oil. Chromatography on alumina with hexane then on silica with dichloromethane-hexane (1:2) yielded 2-benzyl-5-prop-1'-enyl tetrahydrofuran (36b) as a 3:1 diastereomeric mixture. Products were isolated as colourless oils (total yield 50 mg, 55%).

2-Benzyl-5-prop-1'-enyl tetrahydrofuran (36b) $\bar{\nu}_{max}$ (film) 3090, 3060, 3030, 2970, 2940, 2870, 1605, 1500, 1460, 1380, 1360, 1050, 970, 755 and 710 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.5-1.8 (5H, m, $-CH(O)-C\underline{H}_2$ and $=C(H)C\underline{H}_3$), 1.8-2.1 (2H, m, $-CH(O)-C\underline{H}_2$), 2.72 (1H, dd, J 13.4, 7.5 Hz, $-(H)C\underline{H}-Ph$), 3.00 (1H, dd, J 13.4, 5.5 Hz, $-(\underline{H})CH-Ph$), 4.09-4.40 (2H, m, $C\underline{H}-O-C\underline{H}$), 5.47 (1H, m, $-CH-C(\underline{H})=C(H)Me$), 5.66 (1H, dq, J 15.2, 6.4 Hz, $-C(H)=C(\underline{H})CH_3$) and 7.16-7.31 (5H, m, Ar$\underline{H}$); δ_C (22.5 MHz; $CDCl_3$) [major isomer] 17.6, 31.7, 32.8, 42.3,

79.8, 126.2, 127.0, 128.3, 129.4, 132.6 and 138.9; m/z (160°C) 202 (M^+, 5%); 117 (16), 111 (100) and 91 (73). (Found: M^+, 202.1337. $C_{14}H_{18}O$ requires M, 202.1358).

Formation of 6,7-epoxy-11-phenyl-undec-10-enyl-5-oxythiocarbonyl imidazolide (35c) and treatment with $^nBu_3SnH$-AIBN. - 5,6-epoxy-1-phenyl-undec-1-en-7-ol (34c) (126 mg, 0.485 mmol) was dissolved in dry, distilled dichloromethane (10 ml) and N,N'- thiocarbonyl diimidazole (172 mg, 0.965 mmol) was added. The mixture was heated under reflux, with stirring, for 1 h. After cooling, solvent evaporation in vacuo afforded the imidazolide (35c) as an orange oil. This was taken up in dry, deoxygenated THF (50 ml) and the solution was brought to reflux temperature, under nitrogen, with stirring. A solution of tri-n-butyltin hydride (270 µl, 1.00 mmol) and AIBN (10 mg) in THF (1 ml) was added over a period of 1 h, and the mixture was refluxed for a further 15 h. The solvent was removed in vacuo to give an orange oil. Chromatography on alumina with hexane then on silica with dichloromethane-hexane (1:1) yielded 2-benzyl-5-hex-1'enyl tetrahydrofuran (36c) as a 3:1 mixture of diastereoisomers. Products were isolated as colourless liquids (total yield 97 mg, 82%).

2-benzyl-5-hex-1[1]-enyl tetrahydrofuran (36c); $\bar{\nu}_{max}$ (film) 3090, 3060, 3030, 2960, 2930, 2870, 1600, 1500, 1460, 975, 755 and 710 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 0.88 (3H, t, J 7.0 Hz, $CH_2\underline{CH}_3$), 1.32 (4H, m, $-\underline{CH}_2-\underline{CH}_2-CH_3$), 1.60 (2H, m, $=C(H)\underline{CH}_2-$) 1.84-2.03 (4H, m, $-\underline{CH}_2-\underline{CH}_2-$[ring]), 2.71 (1H, dd, J 13.4, 7.6 Hz, $-HC(\underline{H})Ph$), 3.00 (1H, dd, J 13.5, 5.4 Hz, $-\underline{H}C(H)Ph$), 4.07-4.41 (2H, m, $C\underline{H}-O-C\underline{H}$), 5.44 (1H, ddt, J 15.3, 7.2, 1.4 Hz, $-CH-C(\underline{H})=C(H)CH_2-$), 5.65 (1H, dt, J 15.3, 6.6 Hz, $-C(H)=C(\underline{H})CH_2-$) and 7.16-7.31 (5H, m, $Ar\underline{H}$); δ_C (22.5 MHz; $CDCl_3$) 13.9, 22.3, 30.8, 31.4, 31.6, 31.9, 32.9, 42.3, 42.5, 79.9, 81.2, 80.4, 126.2, 128.3, 129.4, 131.2, 132.4 and 138.9; m/z (170°C) 244 (M^+, 1%), 187 (3), 153 (100), 117 (32), 93 (26), 91 (64) and 81 (21). (Found: M^+, 244.1839. $C_{17}H_{24}O$ requires M, 244.1827).

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