1,5-Asymmetric induction in reactions between aldehydes and [(4*S*)-5-(*tert*-butyldimethylsilyloxy)-4-hydroxypent-2-enyl](tributyl)-stannane promoted by tin(IV) chloride

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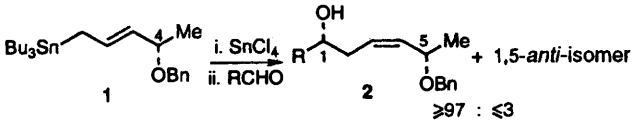
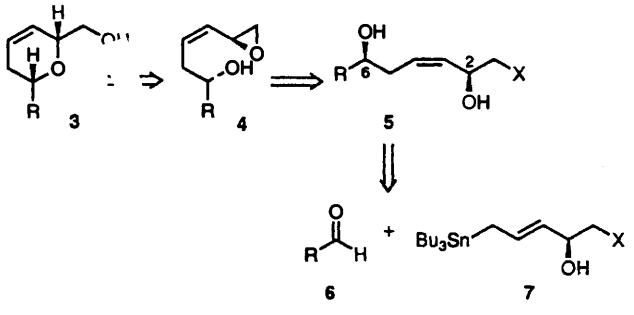
[(4*S*)-5-(*tert*-Butyldimethylsilyloxy)-4-hydroxypent-2-enyl](tributyl)stannane **18** has been prepared from di-*O*-isopropylidene-D-mannitol **8**. Oxidative cleavage of the mannitol derivative followed by condensation with triethyl phosphonoacetate and reduction gave the alcohol **10** which was converted into the xanthate **11**. Deprotection gave the dihydroxy xanthate **12** which was protected as its bis-*tert*-butyldimethylsilyl ether **13**. This rearranged on heating in toluene to give the dithiocarbonate **15** which reacted with tributyltin hydride under free radical conditions to give the [(4*S*)-4,5-bis(*tert*-butyldimethylsilyloxy)pent-2-enyl](tributyl)stannane **16** as an approximately 9:1 mixture of *E*- and *Z*-isomers. Deprotection and selective protection of the primary hydroxy group provided the [(4*S*)-5-(*tert*-butyldimethylsilyloxy)-4-hydroxypent-2-enyl]stannane **18**. As a shorter route, the primary hydroxy group of the dihydroxy xanthate **12** was protected as its *tert*-butyldimethylsilyl ether **14** which underwent clean rearrangement into the dithiocarbonate **19** when heated in toluene. Reaction with tributyltin hydride under free radical conditions then gave the (5-*tert*-butyldimethylsilyloxy-4-hydroxypent-2-enyl)stannane **18**. Treatment of this 4,5-disubstituted pentenylstannane with tin(IV) chloride generated an allyltin trichloride which reacted with aldehydes with excellent 1,5-asymmetric induction to give 1,5-*syn*-products, *e.g.* **20**, **29–31** and **41**. The stereoselectivity of these reactions would appear to be controlled by the 4-hydroxy substituent rather than by the 5-*tert*-butyldimethylsilyl group. Aspects of the chemistry of these products, in particular their conversion into 2,6-disubstituted 5,6-dihydro-2*H*-pyrans, was investigated.

Useful levels of remote asymmetric induction have been observed in tin(IV) chloride promoted reactions of aldehydes and alkoxyalk-2-enyl(trialkyl)stannanes.[1–6] For example, treatment of the [(*S*)-4-benzyloxypent-2-enyl](tributyl)stannane **1** with tin(IV) chloride, followed by addition of an



aldehyde, gives rise to the formation of 1-substituted *syn*-5-benzyloxyhex-3-enols **2** containing less than 3% of their 1,5-*anti*-epimers.[3] Stereoselective transmetallation of the allylstannane to generate an allyltin trichloride in which the electron deficient tin atom is coordinated to the heteroatom of the substituent, is believed to be involved.[2]

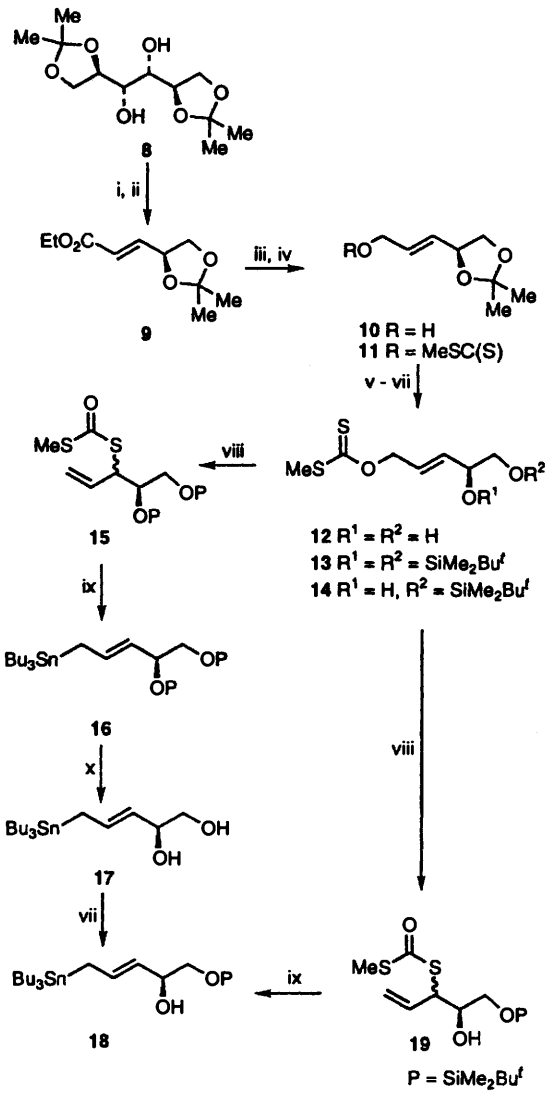
During studies associated with the synthesis of a complex natural product, we wished to synthesize *cis*-2,6-disubstituted 5,6-dihydro-2*H*-pyrans **3**. An approach to these compounds



was envisaged which would involve isomerisation of the unsaturated hydroxy epoxides **4**[7] which in turn would be prepared from the *syn*-alk-3-ene-2,6-diols **5**. By analogy with the stereoselective formation of the 1-substituted 5-benzyloxyhex-3-en-1-ols **2** from tin(IV) chloride promoted reactions between aldehydes and the (4-benzyloxypent-2-enyl)-stannane **1**,[3] the diols **5** would be available stereoselectively from reactions between the 5-substituted 4-hydroxypent-2-enylstannane **7** and aldehydes **6**, if the stereoselectivity of these reactions is controlled by the 4-hydroxy substituent rather than by the 5-substituent. We now report the synthesis of [(4*S*)-5-*tert*-butyldimethylsilyloxy-4-hydroxypent-2-enyl](tributyl)stannane **18** and the stereoselectivity of its reactions with aldehydes. This bifunctionalised stannane was chosen since it was expected that the 4-hydroxy substituent would be more likely to control the stereochemistry of the transmetallation step than the hindered 5-*tert*-butyldimethylsilyloxy substituent and establish the required configuration in the product formed during the reaction with an aldehyde. Attempts are also described to convert the *syn* alk-3-ene-2,6-diols so obtained into 5,6-dihydro-2*H*-pyrans **3**. In the accompanying paper, stereoselective syntheses of *cis*-2,6-disubstituted 5,6-dihydro-2*H*-pyrans **3** and their 2,6-*trans*-stereoisomers based on this chemistry are described.[8]

Results and discussion

[(4*S*)-5-*tert*-Butyldimethylsilyloxy-4-hydroxypent-2-enyl](tributyl)stannane **18** was prepared from 1,2:5,6-di-*O*-isopropylidene-D-mannitol **8** as outlined in Scheme 1. Oxidative cleavage of the mannitol derivative using sodium periodate and trapping the aldehyde so obtained *in situ* by triethyl phosphonoacetate and potassium carbonate gave the unsaturated ester **9** (87% yield from **8**).[9] Reduction using diisobutylaluminium hydride then gave the alcohol **10**,[9] which



Scheme 1 *Reagents and conditions:* i, sodium periodate, sodium hydrogen carbonate; ii, $(EtO)_2P(O)CH_2CO_2Et$, potassium carbonate (87% from **8**); iii, diisobutylaluminium hydride (100%); iv, NaH, carbon disulfide, methyl iodide (100%); v, aq. hydrogen chloride, tetrahydrofuran (88%); vi, *tert*-butyldimethylsilyl trifluoromethanesulfonate, 2,6-lutidine (95%); vii, *tert*-butyldimethylsilyl chloride, triethylamine, 4-dimethylaminopyridine (**14**, 69%; **18**, 80% from **17**); viii, toluene, heat under reflux, 18 h (**15**, 99%); ix, tributyltin hydride, azoisobutyronitrile (**16**, 90%; **18**, 81% from **14**); x, tetrabutylammonium fluoride, tetrahydrofuran (66%)

was converted into its xanthate **11** using sodium hydride, carbon disulfide and methyl iodide.[10] Hydrolysis of the acetonide under acidic conditions[11] gave the dihydroxy xanthate **12** which was protected as its bis-*tert*-butyldimethylsilyl ether **13**.[12] This was rearranged into the dithiocarbonate **15** by heating in toluene under reflux, and treatment with tributyltin hydride under free radical conditions gave the [bis(*tert*-butyldimethylsilyloxy)pent-2-enyl]stannane **16** as a 9:1 mixture of *E*- and *Z*-double-bond isomers.[13] Deprotection of the bis-protected stannane **16** with an excess of tetrabutylammonium fluoride[14] gave the (4,5-dihydroxypent-2-enyl)stannane **17**, which was monosilylated to give the [(4*S*)-5-(*tert*-butyldimethylsilyloxy)-4-hydroxypent-2-enyl]stannane **18**.[15] As an alternative route to this stannane, the dihydroxy xanthate **12** was converted into its mono-*tert*-butyldimethylsilyl ether **14** which was rearranged to the dithiocarbonate **19** by heating in toluene under reflux. Treatment with tributyltin hydride under free radical conditions then gave the 5-(*tert*-butyldimethylsilyloxy)-4-hydroxypent-2-enylstannane **18**, ratio *E*:*Z* = 4:1 (^{1}H NMR).

Reactions between the 5-*tert*-butyldimethylsilyloxy-4-hydroxypen-2-enylstannane **18** and aldehydes were carried out by adding tin(IV) chloride to the stannane at −78 °C, followed by the aldehyde. From benzaldehyde, a mixture of two diols identified as the 1,5-*syn*-diol **20** and its 1,5-*anti*-isomer **21**, ratio 97:3 (HPLC, ^{1}H NMR), yield 86%, was obtained (Scheme 2). The configuration of the major product at C-1 was shown to be *S* by acetylation of the mixture of products followed by ozonolysis and reduction. This gave the laevorotatory 1-phenylpropane-1,3-diol, [α] −57.4 (lit.,[16] −63.8), which is known to correspond to the *S*-enantiomer **23**.[3,16] The double-bond of the major product **20** was assigned the *Z* configuration by ^{1}H NMR, since its 3,4-coupling constant was found to be 11 Hz, and NOE difference spectra showed significant enhancement of 2-H_2 on irradiation of 5-H, and *vice versa*.

To establish the structure of the minor component to confirm that the 1,5-*syn*- and 1,5-*anti*-diastereoisomers were being distinguished, the 1,5-*syn*-product **20** was converted into its 1,5-*anti*-isomer **21** by deprotection and selective acetonide formation,[17] followed by inversion of configuration using a Mitsunobu reaction[18] and saponification. Hydrolysis and selective silylation of the primary hydroxy group gave the 1,5-*anti*-isomer **21** which was distinctly different from its *syn*-epimer by ^{1}H NMR spectroscopy and HPLC.

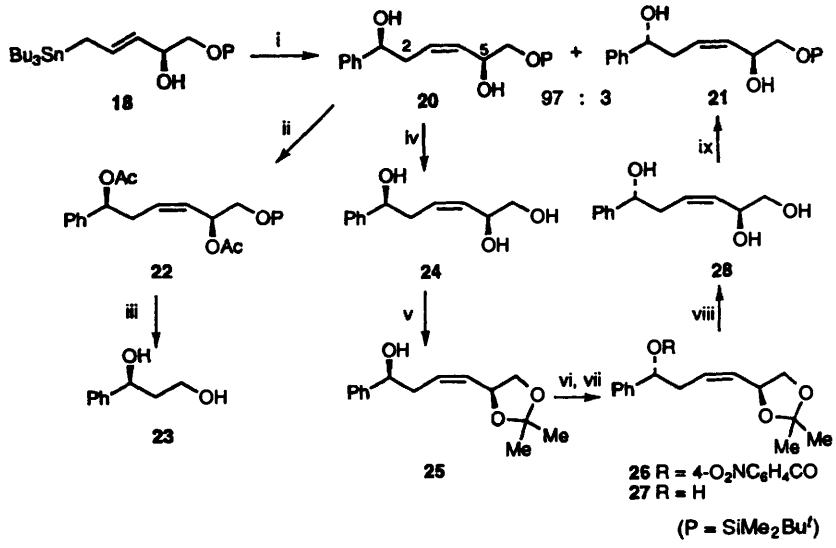
The 4-hydroxypent-2-enylstannane **18** was treated with acrolein, propanal and ethyl glyoxylate; these aldehydes being chosen so that the products could be used to evaluate the proposed synthesis of the 5,6-dihydro-2*H*-pyrans **3**. With acrolein, a good yield of the *syn*-diol **29** containing *ca.* 4% of a minor product, believed to be its *anti*-isomer, was obtained. Propanal gave rise to the formation of a mixture of three products in a ratio of 89:8:3, with the major product being identified as the *syn*-diol **30**. Ethyl glyoxylate reacted slightly less stereoselectively giving a mixture of two products, ratio 86:14, identified as the *syn*-diol **31** together with its *anti*-isomer.

The structures of these products were assigned by analogy with the selective formation of the *syn*-diol **20** from the reaction of the stannane **18** with benzaldehyde, and were consistent with their spectroscopic data. It would appear that the 4-hydroxy-5-(silyloxy)alkenylstannane **18** reacts with aldehydes with useful levels of 1,5-stereoselectivity induced by the 4-hydroxy substituent, the 5-silyloxy group not playing a significant part in influencing the stereochemical outcome of these reactions.

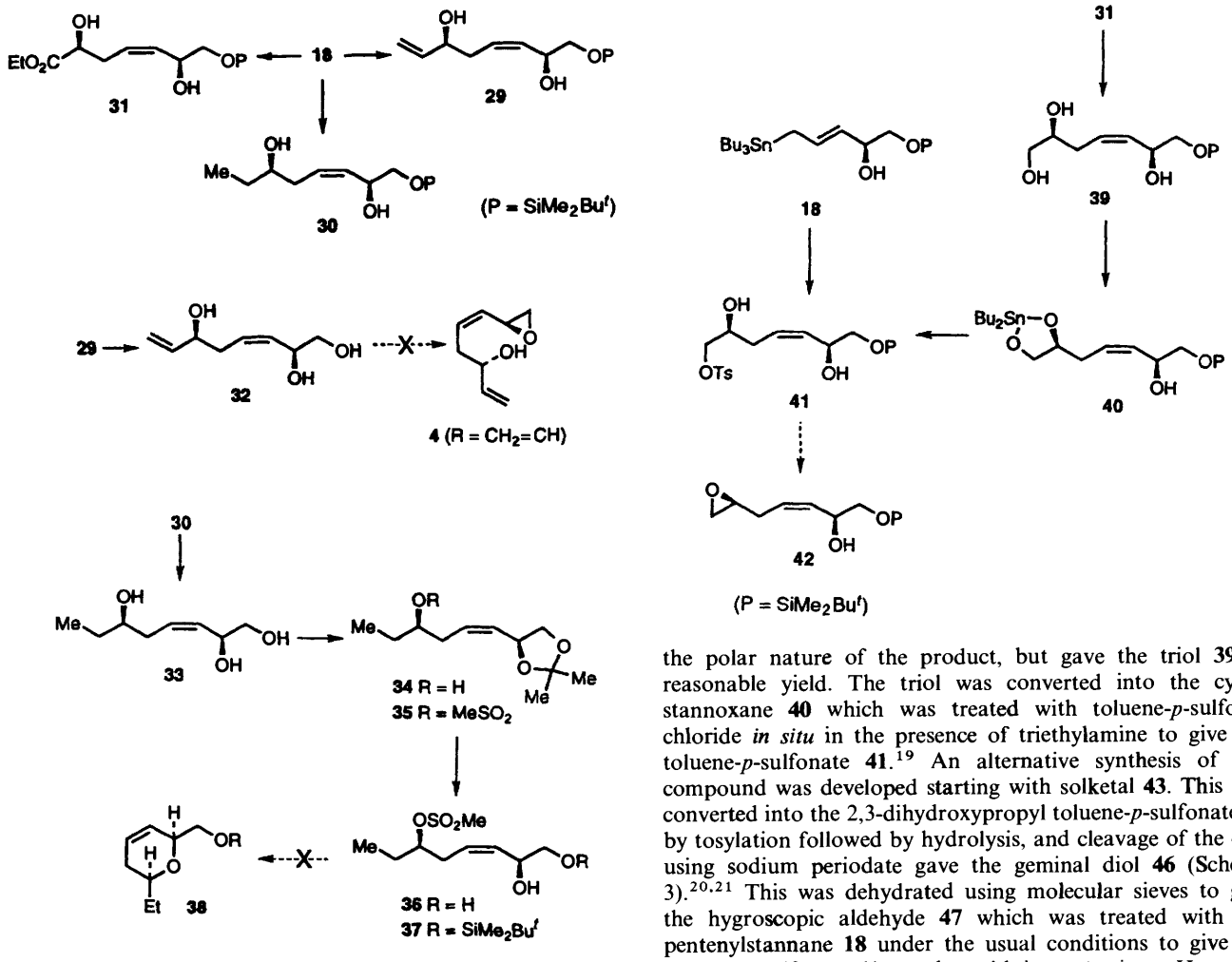
Conversion of the *syn*-1,5-diols **29**–**31** into *cis*-2,6-disubstituted 5,6-dihydro-2*H*-pyrans was briefly investigated. Deprotection of the product **29** obtained from the reaction of the stannane **18** with acrolein gave the triol **32**. However, attempts to convert this into the epoxide **4** (R = CH_2=CH) by selective toluene-*p*-sulfonylation of the primary hydroxy group and cyclisation, or by a Mitsunobu cyclisation of the triol, gave mixtures of polymeric products which could not be characterised. Perhaps these reactions are unsuccessful because the allylic epoxide group is unstable in the presence of the free hydroxy group leading to polymerisation.

As an alternative approach to 5,6-dihydro-2*H*-pyrans, the product **30** from the reaction of the stannane **18** with propanal, was desilylated to give the triol **33** which was protected as its acetonide **34**. Methanesulfonylation followed by hydrolysis and selective silylation of the primary hydroxy group gave the methanesulfonate **37**. However, attempts to cyclise this into the 5,6-dihydro-2*H*-pyran **38** using basic conditions were unsuccessful, unchanged starting material being obtained. It may be that the displacement of the secondary methane sulfonate by a secondary alcohol is inefficient because of steric hindrance.

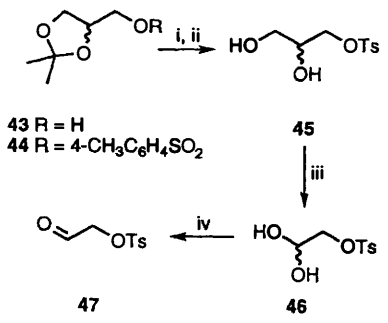
A third approach to 5,6-dihydro-2*H*-pyrans was investigated



Scheme 2 *Reagents and conditions:* i, tin(IV) chloride, −78 °C, 5 min, benzaldehyde, −78 °C, 1 h (86%); ii, acetic anhydride, pyridine (93%); iii, ozone, dimethyl sulfide, then lithium aluminium hydride (77%); iv, tetrabutylammonium fluoride, tetrahydrofuran (96%); v, 2,2-dimethoxypropane, pyridinium toluene-*p*-sulfonate (73%); vi, diisopropyl diazodicarboxylate, triphenylphosphine, 4-nitrobenzoic acid (79%); vii, sodium hydroxide, methanol, water (73%); viii, dilute aqueous hydrogen chloride (94%); ix, *tert*-butyldimethylsilyl chloride, triethylamine, 4-dimethylaminopyridine (67%)



using the *syn*-diol **31** obtained from the reaction of the stannane **18** with ethyl glyoxylate. Reduction of the ester group using diisobutylaluminium hydride was a little capricious because of the polar nature of the product, but gave the triol **39** in reasonable yield. The triol was converted into the cyclic stannoxane **40** which was treated with toluene-*p*-sulfonyl chloride *in situ* in the presence of triethylamine to give the toluene-*p*-sulfonate **41**.[19] An alternative synthesis of this compound was developed starting with solketal **43**. This was converted into the 2,3-dihydroxypropyl toluene-*p*-sulfonate **45** by tosylation followed by hydrolysis, and cleavage of the diol using sodium periodate gave the geminal diol **46** (Scheme 3).[20,21] This was dehydrated using molecular sieves to give the hygroscopic aldehyde **47** which was treated with the pentenylstannane **18** under the usual conditions to give the toluene-*p*-sulfonate **41** together with its *anti*-epimer. However, attempts to convert the toluene-*p*-sulfonate **41** into the epoxide **42** by treatment with potassium carbonate in methanol gave rise to the formation of mixtures of products which may have contained an epoxide, but which could not be separated. It



Scheme 3 *Reagents:* i, 4-dimethylaminopyridine, toluene-*p*-sulfonyl chloride, pyridine; ii, aqueous HCl, tetrahydrofuran (99% from **43**); iii, sodium periodate; iv, 4 Å molecular sieves (77%)

appeared that both the 2- and 6-hydroxy groups were participating in displacement of the toluene-*p*-sulfonyloxy group leading to the formation of mixtures of isomeric products.

It appears that the use of products prepared from the 4-hydroxypentenylstannane **18** for the synthesis of 5,6-dihydro-2*H*-pyrans is not straightforward because the free hydroxy group derived from the stannane can lead to the formation of mixtures of products. Although these investigations could have been pursued, they were discontinued when a parallel study using a derivative of the 4-hydroxypentenylstannane **18** resulted in the successful stereoselective synthesis of 2,6-disubstituted 5,6-dihydro-2*H*-pyrans. This work is described in the accompanying paper.[8] Nevertheless, the work described in this paper shows that the useful 1,5-asymmetric induction observed during reactions between 5-alkoxypentenylstannanes and aldehydes is also found in the analogous reactions of the 4,5-disubstituted pent-2-enylstannane **18** and extends the use of this chemistry for stereoselective synthesis.

Experimental

All non-aqueous reactions were carried out under an atmosphere of dry nitrogen or argon. ^1H and ^{13}C NMR spectra were recorded on Bruker AC 300, Varian XL 300 and Varian Gemini 200 spectrometers in [^2H]chloroform unless otherwise stated. *J* Values are in Hz. IR spectra were measured on a Perkin-Elmer 1710FT spectrometer as evaporated films unless otherwise stated. Mass spectra were recorded on Kratos MS25, Kratos Concept and Fisons VG Trio 2000 mass spectrometers using electron impact (EI) or chemical ionisation (CI) modes. Chromatography refers to flash column chromatography on Merck silica 60 H (40–60μm, 230–300 mesh) or Sorbsil C60 silica gel. Analytical HPLC was performed using a C18 Novapak cartridge (8 mm × 100 mm) with a Perkin-Elmer diode array system for detection at 254 nm. All solvents were dried by standard procedures and distilled before use. Light petroleum refers to the fraction which distils at 40–60 °C. Ether refers to diethyl ether. $[\alpha]_D$ Values are given in units of 10^{-1} deg cm^2 g^{-1}. Ethyl (4*S*,2*E*)-4,5-isopropylidenedioxypent-2-enoate **9** was prepared and reduced to (4*S*,2*E*)-4,5-isopropylidenedioxypent-2-enol **10** as described in the literature.[9]

(4*S*,2*E*)-*O*-4,5-Isopropylidenedioxypent-2-enyl *S*-methyl dithiocarbonate 11

A solution of alcohol **10** (64.1 g, 0.41 mol) in toluene (640 cm^3) was added to a suspension of sodium hydride (60% dispersion in oil; 16.2 g) in toluene (1250 cm^3) at 0 °C. The solution was allowed to warm to ambient temperature and stirred for 90 min before being cooled to 0 °C. Carbon disulfide (98.8 cm^3, 1.64 mol) was added dropwise to it and then the reaction mixture was allowed to warm to ambient temperature. The mixture was stirred for 4 h, cooled to 0 °C and then iodomethane (100 cm^3, 1.61 mol) was added dropwise to it. The mixture was then allowed to warm to ambient temperature and was stirred for 18 h. The mixture was filtered through Celite and the precipitate washed with CH_2Cl_2. The organic extracts were concentrated under reduced pressure to afford the *title compound* **11** (99.5 g, 100%). This was used without purification, but a small portion was chromatographed on silica gel using light petroleum–ether (10:1) as eluent for characterisation (Found: $M^+ + NH_4$, 266.0877. $C_{10}H_{20}NO_3S_2$ requires *M*, 266.0885); $[\alpha]_D^{22}$ +22.3 (*c* 2.6, $CHCl_3$); ν_{max}/cm^{-1} 1648, 1213, 1156, 1062 and 863; δ_H 1.43 and 1.47 (each 3 H, s, CH_3CCH_3), 2.61 (3 H, s, SCH_3), 3.66 (1 H, t, *J* 8, 5-H), 4.16 (1 H, dd, *J* 8, 6, 5-H′), 4.59 (1 H, q, *J* 7, 4-H), 5.14 (2 H, d, *J* 6, 1-H_2), 5.88 (1 H, dd, *J* 15, 7, 3-H) and 6.04 (1 H, dt, *J* 15, 7, 2-H); δ_C 19.1, 25.8, 26.7, 69.3, 72.7, 76.0, 109.6, 126.4, 133.3 and 215.5; *m*/*z* (CI) 266 ($M^+ + NH_4$, 100%), 249 ($M^+ + H$, 51), 208 (18) and 191 (63).

(4*S*,2*E*)-*O*-4,5-Dihydroxypent-2-enyl *S*-methyl dithiocarbonate 12

Dilute hydrochloric acid (1 mol dm^{-3}; 400 cm^3) was added dropwise to a solution of xanthate **11** (99 g, 0.4 mol) in tetrahydrofuran (1200 cm^3) at 0 °C. The solution was allowed to warm to ambient temperature and stirred for 18 h then cooled to 0 °C and saturated aqueous $NaHCO_3$ was added dropwise to it until effervescence ceased. The aqueous phase was extracted with ethyl acetate and the combined organic extracts washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure to give a viscous oil which was triturated with pentane to afford the *title compound* **12** as an amorphous yellow solid (73.1 g, 88%). A portion was purified for characterisation by chromatography on silica gel using light petroleum–ethyl acetate (1:2) as eluent (Found: $M^+ + NH_4$, 226.0571. $C_7H_{16}NO_3S_2$ requires *M*, 226.0572); $[\alpha]_D^{22}$ +3.4 (*c* 2.3, $CHCl_3$); ν_{max}/cm^{-1} 3362, 1644, 1422, 1219, 1060, 969 and 872; δ_H 2.53 (3 H, s, SCH_3), 2.96 and 3.23 (each 1 H, br s, OH), 3.48 and 3.67 (each 1 H, m, 5-H), 4.28 (1 H, m, 4-H), 5.09 (2 H, d, *J* 6, 1-H_2), 5.83 (1 H, dd, *J* 16, 5, 3-H) and 5.98 (1 H, dtd, *J* 16, 7, 1.5, 2-H); δ_C 19.3, 66.1, 72.2, 73.0, 125.1, 134.0 and 215.3; *m*/*z* (CI) 226 ($M^+ + NH_4$, 100%), 209 ($M^+ + H$, 8), 195 (9) and 178 (68).

(4*S*,2*E*)-*O*-4,5-Bis(*tert*-butyldimethylsilyloxy)pent-2-enyl *S*-methyl dithiocarbonate 13

tert-Butyldimethylsilyl trifluoromethanesulfonate (1.45 cm^3, 8.28 mmol) was added to a solution of diol **12** (0.6 g, 2.88 mmol) and 2,6-lutidine (2,6-dimethylpyridine) (1.65 cm^3, 14.1 mmol) in dichloromethane (10 cm^3) at 0 °C. The mixture was stirred at 0 °C for 5 min and then allowed to warm to ambient temperature and stirred for 30 min. The mixture was cooled to 0 °C, and saturated aqueous $NaHCO_3$ (5 cm^3) was added dropwise to it. The mixture was extracted with ethyl acetate and the organic extracts were washed with water and brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (20:1) as eluent gave the *title compound* **13** as a pale yellow oil (1.20 g, 95%) (Found: $M^+ + NH_4$, 454.2297. $C_{19}H_{44}NO_3S_2Si_2$ requires *M*, 454.2301); $[\alpha]_D^{22}$ −7.7 (*c* 1.6, $CHCl_3$); ν_{max}/cm^{-1} 2857, 1472, 1255, 1218, 1062, 836 and 777; δ_H 0.09 [6 H, s, $Si(CH_3)_2$], 0.11 and 0.12 (each 3 H, s, $SiCH_3$), 0.94 and 0.95 [each 9 H, s, $SiC(CH_3)_3$], 2.60 (3 H, s, SCH_3), 3.49 and 3.61 (each 1 H, dd, *J* 10, 6, 5-H), 4.28 (1 H, m, 4-H), 5.14 (2 H, m, 1-H_2) and 5.97 (2 H, m, 2-H and 3-H); δ_C −5.3, −5.2, −4.7, 18.3, 18.4, 19.0, 25.9, 26.0, 67.7, 73.2, 73.6, 123.2, 137.1 and 215.5; *m*/*z* (CI) 454 ($M^+ + NH_4$, 89%), 329 (94), 305 (81) and 214 (100).

(4*S*,2*E*)-*O*-5-(*tert*-Butyldimethylsilyloxy)-4-hydroxypent-2-enyl *S*-methyl dithiocarbonate 14

tert-Butyldimethylsilyl chloride (58.0 g, 0.385 mol) in dichloromethane (500 cm^3) was added dropwise to a solution of diol **12** (72.1 g, 0.347 mol), triethylamine (53 cm^3, 0.380 mol), and 4-dimethylaminopyridine (2.1 g, 0.017 mol) in dichloromethane (600 cm^3) at 0 °C over 2 h. The solution was allowed to warm to ambient temperature and stirred for 18 h before being cooled to 0 °C after which brine (200 cm^3) was added dropwise to it. The aqueous phase was extracted with ethyl acetate and the organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography on silica gel using gradient elution with pentane–ether (30:1 to 5:1) as eluent, gave the *title compound* **14** as a yellow oil (76.8 g, 69%) (Found: $M^+ + NH_4$, 340.1432. $C_{13}H_{30}NO_3S_2Si$ requires *M*, 340.1436); $[\alpha]_D^{22}$ −4.1 (*c* 2.1, $CHCl_3$); ν_{max}/cm^{-1} 3460, 2858, 1740, 1649, 1257, 1117 and 837; δ_H 0.1 [6 H, s, $Si(CH_3)_2$], 0.93 [9 H, s, $SiC(CH_3)_3$], 2.54 (3 H, s, SCH_3), 2.62 (1 H, d, *J* 3.5, OH), 3.44 (1 H, dd, *J* 10, 7.5, 5-H), 3.66 (1 H, dd, *J* 10, 4, 5-H), 4.22 (1 H, m, 4-H), 5.08 (2 H, d, *J* 6, 1-H_2), 5.81 (1 H, dd, *J* 16, 5.5, 3-H) and 5.99 (1 H, dtd, *J* 16, 6, 1.5, 2-H); δ_C −5.2, 18.4, 19.2, 25.9, 66.7, 71.8, 73.2, 124.7, 134.1 and 215.2; *m/z* (CI) 340 ($M^+ + NH_4$, 94%), 323 ($M^+ + H$, 16), 293 (18) and 292 (100).

[(4*S*)-4,5-Bis(*tert*-butyldimethylsilyloxy)pent-2-enyl]-(tributyl)stannane 16

A solution of xanthate **13** (1.20 g, 2.75 mmol) in toluene (10 cm^3) was heated under reflux for 18 h. The solution was cooled and the solvent removed under reduced pressure to give the dithiocarbonate **15** as a mixture of epimers (1.19 g, 99%); ν_{max}/cm^{-1} 2858, 1649, 1256, 1118, 864, 835 and 777; δ_H 0.04 (9 H, br s, 3 × $SiCH_3$), 0.11 (3 H, s, $SiCH_3$), 0.88 [18 H, m, 2 × $SiC(CH_3)_3$], 2.38 (1 H, s, SCH_3), 2.39 (2 H, s, SCH_3), 3.45 (2 H, m, 5-H_2), 3.88 (1 H, m, 4-H), 4.55 (1 H, m, 3-H), 5.11 (0.33 H, m, 1-H), 5.16 (0.66 H, m, 1-H), 5.31 (1 H, m, 1-H′) and 5.87 (1 H, m, 2-H).

The dithiocarbonate **15** (1.19 g, 2.73 mmol) was dissolved in benzene (14 cm^3) and the solution degassed with nitrogen for 90 min at ambient temperature. Tributyltin hydride (0.902 cm^3, 3.35 mmol) and azoisobutyronitrile (AIBN) (cat.) were added, and the solution was heated under reflux for 4 h. The mixture was cooled and concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ether (100:1, 1% triethylamine) as eluent, gave the *title compound* **16** (1.53 g, 90%), as an approximately 4:1 mixture of *E*- and *Z*-isomers (Found: $M^+ - C_4H_9$, 563.2758. $C_{25}H_{55}O_2Si_2{}^{120}Sn$ requires *M*, 563.2763); ν_{max}/cm^{-1} 2857, 1464, 1254, 1125, 1077, 836 and 777; δ_H 0.09 and 0.10 [each 6 H, s, $Si(CH_3)_2$], 0.93 [33 H, m, 2 × $SiC(CH_3)_3$ and $(CH_3CH_2CH_2CH_2)_3Sn$], 1.20–1.90 [14 H, m, $(CH_3CH_2CH_2CH_2)_3Sn$ and 1-H_2], 3.45 (1 H, dd, *J* 10, 5.5, 5-H), 3.53 (1 H, dd, *J* 10, 7, 5-H′), 4.14 (1 H, m, 4-H), 5.25 (1 H, dd, *J* 15, 6.5, 3-H) and 5.81 (1 H, dt, *J* 15, 8, 2-H); *m/z* (EI) 563 ($M^+ - Bu$, 4%), 365 (38), 363 (35) and 291 (100).

[(2*S*)-4,5-Dihydroxypent-2-enyl](tributyl)stannane 17

Tetrabutylammonium fluoride (1.1 mol dm^{-3} in tetrahydrofuran; 6.2 cm^3) was added dropwise to a solution of stannane **16** (1.28 g, 3.27 mmol) in tetrahydrofuran (22 cm^3) at 0 °C. The solution was allowed to warm to ambient temperature and stirred for 7 h. Brine (5 cm^3) was added to it and the mixture stirred for 30 min before being extracted with ethyl acetate. The combined organic extracts were dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (2:1, 1% triethylamine) as eluent gave the *title compound* **17** as a colourless oil (0.54 g, 66%) (Found: $M^+ - Bu$, 335.1036. $C_{13}H_{27}O_2{}^{120}Sn$ requires *M*, 335.1033); ν_{max}/cm^{-1} 3373, 1655, 1463, 1073 and 873; δ_H 0.93 [15 H, m, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.34 [6 H, m, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.51 [6 H, m, $(CH_3CH_2CH_2CH_2)_3Sn$], 1.79 (2 H, d, *J* 9, 1-H_2), 1.96 and 2.06 (each 1 H, br s, OH), 3.51 and 3.62 (each 1 H, m, 5-H), 4.19 (1 H, m, 4-H), 5.27 (1 H, dd, *J* 15, 7.5, 3-H) and 5.96 (1 H, dt, *J* 15, 6.5, 2-H); δ_C 9.3, 13.7, 14.7, 27.3, 29.0, 67.0, 73.8, 123.2 and 134.8; *m/z* (EI) 361 (56%), 359 (62), 335 ($M^+ - C_4H_9$, 49), 317 (40), 291 (95) and 235 (100).

[(4*S*)-5-(*tert*-Butyldimethylsilyloxy)-4-hydroxypent-2-enyl](tributyl)stannane 18

From xanthate 14. A solution of xanthate **14** (10.27 g, 31.9 mmol) in toluene (170 cm^3) was heated under reflux for 18 h. The solution was cooled and an aliquot removed and concentrated under reduced pressure to give the dithiocarbonate **19** as a pale yellow oil; ν_{max}/cm^{-1} 3407, 2858, 1730, 1648, 1256, 1116 and 869; δ_H 0.01 [6 H, s, $Si(CH_3)_2$], 0.83 [9 H, s, $SiC(CH_3)_3$], 2.35 (3 H, s, SCH_3), 3.56 (2 H, m, 5-H_2), 3.75 and 3.82 (each 0.5 H, m, 4-H), 4.31 (1 H, m, 3-H), 5.13 (1 H, m, 1-H), 5.28 (1 H, m, 1-H′) and 5.83 (1 H, m, 2-H).

The remainder of the solution was degassed with nitrogen for 1 h and tributyltin hydride (16 cm^3, 59.5 mmol) and AIBN (cat.) were added to it. The mixture was heated under reflux for 4 h and cooled, filtered and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ether (20:1, 1% triethylamine) as eluent, gave the *title compound* **18** as a colourless oil (12.92 g, 81%) (Found: $M^+ - Bu$, 449.1892. $C_{19}H_{41}O_2Si{}^{120}Sn$ requires *M*, 449.1897); ν_{max}/cm^{-1} 3464, 1656, 1463, 1254, 1106, 838 and 779; δ_H 0.12 [6 H, s, $Si(CH_3)_2$], 0.94 [24 H, m, $SiC(CH_3)_3$ and $(CH_3CH_2CH_2CH_2)_3Sn$], 1.20–1.90 [14 H, m, $(CH_3CH_2CH_2CH_2)_3Sn$ and 1-H_2], 2.54 (1 H, d, *J* 2.5, OH), 3.42 (1 H, dd, *J* 10, 7, 5-H), 3.61 (1 H, dd, *J* 10, 3.5, 5-H), 4.11 (0.8 H, m, 4-H), 4.49 (0.2 H, m, 4-H), 5.06 (0.2 H, m, 3-H), 5.22 (0.8 H, dd, *J* 15, 7.5, 3-H), 5.80 (0.2 H, q, *J* 9.5, 2-H) and 5.93 (0.8 H, dt, *J* 15, 7, 2-H); *m/z* (EI) 453 ($M^+ - C_4H_9$, 1.4%), 449 ($M^+ - C_4H_9$, 6), 445 (3), 291 (56) and 235 (80).

From dihydroxystannane 17. *tert*-Butyldimethylsilyl chloride (0.11 g, 0.76 mmol) was added to a solution of the dihydroxystannane **17** (0.27 g, 0.69 mmol), triethylamine (0.11 cm^3, 0.76 mmol) and 4-dimethylaminopyridine (cat.) in dichloromethane (1.5 cm^3) at 0 °C. The solution was allowed to warm to ambient temperature and stirred for 18 h. Brine (1.5 cm^3) was added to the mixture, and the aqueous phase extracted with ethyl acetate. The organic extracts were dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ether (20:1, 1% triethylamine) as eluent, afforded the *title compound* as a colourless oil (0.28 g, 80%).

General procedure for the reactions of stannane 18 with aldehydes

Tin(IV) chloride (1 mol dm^{-3} in dichloromethane) was added dropwise to a solution of the stannane **18** (0.1–0.5 mol dm^{-3}; 1 mol equiv.) in dichloromethane at −78 °C. The solution was stirred at −78 °C for 5 min before the aldehyde (1–2 mol equiv.) in dichloromethane was added to it. The solution was stirred at −78 °C for 1 h, then saturated aqueous $NaHCO_3$ was added to it, and the mixture allowed to warm to ambient temperature and then extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ethyl acetate (1% triethylamine) as eluent, afforded the products as colourless oils. The following compounds were prepared using this procedure.

(1*S*,5*S*,3*Z*)-6-(*tert*-Butyldimethylsilyloxy)-1-phenylhex-3-ene-1,5-diol 20. (0.26 g, 86%) (Found: $M^+ + NH_4$, 340.2293. $C_{18}H_{34}NO_3Si$ requires *M*, 340.2308); $[\alpha]_D^{22}$ −28.2 (*c* 2.5, $CHCl_3$); ν_{max}/cm^{-1} 3361, 2857, 1471, 1255, 1113, 1055, 837, 779

and 700; δ_H 0.1 [6 H, s, $Si(CH_3)_2$], 0.95 [9 H, s, $SiC(CH_3)_3$], 2.50 (1 H, m, 2-H), 2.72 (1 H, dt, *J* 14, 8.5, 2-H'), 3.05 and 3.21 (each 1 H, br s, OH), 3.46 (1 H, dd, *J* 10, 8, 6-H), 3.53 (1 H, dd, *J* 10, 4.5, 6-H), 4.45 (1 H, td, *J* 8, 4.5, 5-H), 4.72 (1 H, dd, *J* 8, 4.5, 1-H), 5.59 (1 H, dd, *J* 11, 8, 4-H), 5.72 (1 H, m, 3-H) and 7.38 (5 H, m, ArH); δ_C −5.3, −5.2, 18.4, 25.9, 38.4, 66.6, 67.8, 73.0, 125.8, 127.5, 128.4, 130.3, 131.2 and 144.3; *m/z* (CI) 340 ($M^+ + NH_4$, 58%) and 322 (M^+, 100).

(2*S*,6*S*,3*Z*)-1-(*tert*-Butyldimethylsilyloxy)octa-3,7-diene-2,6-diol 29. (2.39 g, 87%) (Found: $M^+ + NH_4$, 290.2151. $C_{14}H_{32}NO_3Si$ requires *M*, 290.2151); $[\alpha]_D^{22}$ +31.5 (*c* 2.9, $CHCl_3$); ν_{max}/cm^{-1} 3362, 2858, 1471, 1255, 1118, 1060, 837 and 778; δ_H 0.10 [6 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 2.33 (1 H, dt, *J* 13, 6, 5-H), 2.47 (1 H, dt, *J* 14, 8, 5-H), 2.97 and 3.10 (each 1 H, br s, OH), 3.54 (1 H, dd, *J* 10, 7, 1-H), 3.62 (1 H, dd, *J* 10, 4, 1-H'), 4.15 and 4.46 (each 1 H, m, 2-H and 6-H), 5.14 (1 H, d, *J* 10.5, 8-H), 5.28 (1 H, d, *J* 17, 8-H'), 5.57 (1 H, dd, *J* 11, 8, 3-H), 5.67 (1 H, m, 4-H) and 5.91 (1 H, ddd, *J* 17, 10.5, 5.5, 7-H); δ_C −5.4, −5.3, 18.3, 25.9, 35.9, 66.7, 67.9, 71.6, 114.8, 130.0, 131.1 and 140.5; *m/z* (CI) 290 ($M^+ + NH_4$, 24%), 272 (M^+, 29) and 255 (100).

(2*S*,6*R*,3*Z*)-1-(*tert*-Butyldimethylsilyloxy)oct-3-ene-2,6-diol 30. (0.4 g, 75%) (Found: $M^+ + NH_4$, 292.2313. $C_{14}H_{34}NO_3Si$ requires *M*, 292.2308); $[\alpha]_D^{22}$ +38.0 (*c* 1.4, $CHCl_3$); ν_{max}/cm^{-1} 3365, 2858, 1464, 1256, 1116, 838 and 779; δ_H 0.09 [6 H, s, $Si(CH_3)_2$], 0.93 [9 H, s, $SiC(CH_3)_3$], 0.99 (3 H, t, *J* 7.5, 8-H_3), 1.56 (2 H, m, 7-H_2), 2.27 (1 H, m, 5-H), 2.38 (1 H, dt, *J* 14, 9, 5-H'), 2.52 and 3.02 (1 H, br s, OH), 3.53 (1 H, dd, *J* 10, 8, 1-H), 3.55 (1 H, m, 6-H), 3.64 (1 H, dd, *J* 10, 4, 1-H), 4.47 (1 H, td, *J* 7.5, 4, 2-H), 5.58 (1 H, dd, *J* 11.5, 8, 3-H) and 5.72 (1 H, m, 4-H); δ_C −5.4, −5.3, 10.0, 18.3, 25.9, 30.1, 35.5, 66.7, 67.8, 71.9, 130.8 and 130.9; *m/z* (CI) 292 ($M^+ + NH_4$, 52%), 274 (M^+, 50) and 257(100).

Ethyl (2*S*,6*S*,4*Z*)-7-(*tert*-butyldimethylsilyloxy)-2,6-dihydroxyhept-4-enoate 31. (0.2 g, 78%) (Found: $M^+ + NH_4$, 336.2226. $C_{15}H_{34}NO_5Si$ requires *M*, 336.2206); ν_{max}/cm^{-1} 3410, 2858, 1736, 1255, 1207, 1112, 838 and 779; δ_H 0.12 [6 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 1.34 (3 H, t, *J* 7, OCH_2CH_3), 2.64 (2 H, t, *J* 6, 3-H_2), 3.52 (1 H, dd, *J* 10, 8, 7-H), 3.66 (1 H, dd, *J* 10, 4, 7-H'), 4.35 (3 H, m, OCH_2CH_3 and 2-H), 4.48 (1 H, td, *J* 8, 4, 6-H), 5.61 (1 H, dd, *J* 11, 6.5, 5-H) and 5.67 (1 H, dt, *J* 11, 6.5, 4-H); δ_C −5.4, −5.3, 14.2, 18.3, 25.9, 32.8, 61.9, 66.6, 68.1, 69.6, 127.7, 132.1 and 174.3; *m/z* (CI) 336 ($M^+ + NH_4$, 65%), 318 (M^+, 70), 301 (56), 290 (91) and 169 (100).

(1*S*,6*S*,3*Z*)-1,5-Diacetoxy-6-(*tert*-butyldimethylsilyloxy)-1-phenylhex-3-ene 22

Acetic anhydride (0.266 cm^3, 2.82 mmol) was added dropwise to a solution of the diol **20** (0.083 g, 0.26 mmol) in pyridine (1 cm^3) and 4-dimethylaminopyridine (cat.) at 0 °C. The mixture was allowed to warm to ambient temperature and was stirred for 3 h. The solution was cooled to 0 °C and saturated aqueous $NaHCO_3$ (1 cm^3) was added to it. The mixture was extracted with ethyl acetate and the organic extracts were washed with saturated aqueous $CuSO_4$, water and brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (8:1) as eluent gave the *title compound* **22** (0.097 g, 93%) (Found: $M^+ + NH_4$, 424.2518. $C_{22}H_{38}NO_5Si$ requires *M*, 424.2519); $[\alpha]_D^{22}$ +43.7 (*c* 0.8, $CHCl_3$); ν_{max}/cm^{-1} 2858, 1740, 1371, 1236, 1026 and 838; δ_H 0.01 [6 H, s, $Si(CH_3)_2$], 0.86 [9 H, s, $SiC(CH_3)_3$], 2.01 and 2.05 (each 3 H, s, CH_3CO), 2.68 and 2.81 (each 1 H, m, 2-H), 3.37 (1 H, dd, *J* 11, 4, 6-H), 3.47 (1 H, dd, *J* 11, 7, 6-H), 5.38 (1 H, m, 3-H), 5.43–5.58 (2 H, m, 4-H and 5-H), 5.76 (1 H, t, *J* 7, 1-H) and 7.31 (5 H, m, ArH); δ_C −5.2, 18.4, 21.3, 25.9, 35.2, 64.5, 70.9, 75.0, 126.5, 127.5, 127.9, 128.3, 129.4, 139.7, 169.9 and 170.0; *m/z* (CI) 424 ($M^+ + NH_4$, 100%), 347 (18), 288 (26) and 287 (92).

A stream of ozone in oxygen was bubbled through a solution of the acetate **22** (0.097 g, 0.24 mmol) in dichloromethane (5 cm^3) at −78 °C for 20 min until a blue coloration persisted. A stream of oxygen was then bubbled through the solution for 5 min until the blue coloration was discharged. Methyl sulfide (0.5 cm^3, 6.81 mmol) was added to the mixture dropwise at −78 °C and the mixture was then allowed to warm to ambient temperature. Concentration under reduced pressure gave a residue which was dissolved in dry ether (2 cm^3) and the solution added dropwise to a suspension of lithium aluminium hydride (0.073 g, 1.92 mmol) in ether (2 cm^3) at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 18 h, then cooled to 0 °C, and aqueous hydrogen chloride (2 cm^3) added dropwise to it. The mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using ethyl acetate–dichloromethane (2:3) as eluent, afforded (*S*)-1-phenylpropane-1,3-diol **23** (28 mg, 77%) (Found: $M^+ + NH_4$, 170.1179. $C_9H_{16}NO_2$ requires *M*, 170.1181); $[\alpha]_D^{22}$ −57.4 (*c* 0.6, $CHCl_3$) (lit.,[16] −63.8); ν_{max}/cm^{-1} 3342, 1494, 1453, 1050, 760 and 701; δ_H 2.05 (2 H, m, 2-H_2), 2.54 and 2.98 (each 1 H, br s, OH), 3.90 (2 H, t, *J* 6, 3-H_2), 5.00 (1 H, dd, *J* 8.5, 4, 1-H) and 7.35 (5 H, m, ArH); *m/z* (CI) 170 ($M^+ + NH_4$, 68%) and 152 (M^+, 100).

(2*S*,6*S*,3*Z*)-6-Phenylhex-3-ene-1,2,6-triol 24

Tetrabutylammonium fluoride (1 mol dm^{-3} in tetrahydrofuran; 1 cm^3) was added dropwise to a solution of the silyl ether **20** (0.21 mg, 0.65 mmol) in tetrahydrofuran (5 cm^3) at 0 °C. The solution was allowed to warm to ambient temperature and stirred for 18 h. Methanol (2 cm^3) and water (0.1 cm^3) were added to it and the mixture was stirred for a further 30 min. The solution was dissolved in ethyl acetate, washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using ethyl acetate as eluent afforded the *title compound* **24** (0.130 g, 96%) (Found: $M^+ + NH_4$, 226.1445. $C_{12}H_{20}NO_3$ requires *M*, 226.1443); $[\alpha]_D^{22}$ −80.4 (*c* 2.3, $CHCl_3$); ν_{max}/cm^{-1} 3347, 1453, 1028, 872 and 760; δ_H 2.41 (1 H, dt, *J* 14, 4, 5-H), 2.70 (1 H, dt, *J* 14, 9, 5-H), 3.40 (1 H, br s, OH), 3.50 (2 H, m, 1-H_2), 4.00 (2 H, br s, 2 × OH), 4.50 (1 H, m, 2-H), 4.69 (1 H, dd, *J* 13.5, 3.5, 6-H), 5.65 (2 H, m, 3-H and 4-H) and 7.38 (5 H, m, ArH); δ_C 37.9, 65.9, 67.8, 72.9, 125.7, 127.7, 128.8, 130.2, 131.5 and 144.0; *m/z* (CI) 226 ($M^+ + NH_4$, 11%) and 208 (M^+, 100).

(1*S*,5*S*,3*Z*)-5,6-Isopropylidenedioxy-1-phenylhex-3-enol 25

A catalytic amount of pyridinium toluene-*p*-sulfonate was added to a solution of triol **24** (95 mg, 0.46 mmol) in 2,2-dimethoxypropane (1 cm^3) and dry *N*,*N*-dimethylformamide (0.5 cm^3) and the solution was stirred for 18 h at ambient temperature. The mixture was dissolved in ethyl acetate (15 cm^3) and washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel, using light petroleum–ethyl acetate (3:1) as eluent, afforded the *title compound* **25** (82 mg, 73%) (Found: $M^+ +$ [NH_4, 266.1752. $C_{15}H_{24}NO_3$ requires *M*, 226.1756); $[\alpha]_D^{22}$ −70.0 (*c* 2.3, $CHCl_3$); ν_{max}/cm^{-1} 3439, 1372, 1215, 1156, 1057 and 860; δ_H 1.41 and 1.44 (each 3 H, s, CH_3CCH_3), 2.58 (2 H, m, 2-H and OH), 2.68 (1 H, dt, *J* 14, 6.5, 2-H'), 3.42 (1 H, t, *J* 8, 6-H), 3.84 (1 H, dd, *J* 8 and 6, 6-H'), 4.73 (2 H, m, 1-H and 5-H), 5.58 (1 H, dd, *J* 11, 8, 4-H), 5.70 (1 H, dt, *J* 11, 7.5, 5-H) and 7.38 (5 H, m, ArH); δ_C 25.9, 26.7, 38.1, 69.2, 71.7, 73.5, 109.2, 125.9, 127.7, 128.5, 130.3, 130.4 and 143.9; *m/z* (CI) 266 ($M^+ + NH_4$, 21), 248 (M^+, 14), 231 (100) and 208 (83)

(1*R*,5*S*,3*Z*)-5,6-Isopropylidenedioxy-1-phenylhex-3-enyl 4-nitrobenzoate 26

Diisopropyl diazodicarboxylate (1.8 cm^3, 8.85 mmol) was

added dropwise to a solution of the alcohol **25** (0.44 g, 1.77 mmol), triphenylphosphine (2.33 g, 8.85 mmol) and 4-nitrobenzoic acid (1.30 g, 7.79 mmol) in toluene (25 cm^3) at −30 °C. The mixture was allowed to warm slowly to ambient temperature and stirred for 18 h. The solution was filtered through a silica plug, the plug was washed with ethyl acetate, and then the filtrate was concentrated under reduced pressure. The residue was adsorbed onto silica, and chromatography using light petroleum–ethyl acetate (10:1) as eluent, gave the *title compound* **26** (0.6 g, 79%); $[\alpha]_D^{22}$ −28.3 (*c* 1.6, $CHCl_3$); ν_{max}/cm^{-1} 1726, 1607, 1529, 1272, 1102, 1059 and 848; δ_H 1.41 and 1.44 (each 3 H, s, CH_3CCH_3), 2.91 (2 H, m, 2-H_2), 3.43 (1 H, t, *J* 8, 6-H), 3.91 (1 H, dd, *J* 8, 6, 6-H), 4.77 (1 H, q, *J* 7, 5-H), 5.59 (1 H, dd, *J* 11, 7, 4-H), 5.67 (1 H, dt, *J* 11, 7, 3-H), 6.11 (1 H, t, *J* 6.5, 1-H), 7.42 (5 H, m, ArH) and 8.27 and 8.34 (each 2 H, d, *J* 9.5, ArH); δ_C 25.9, 26.7, 34.6, 69.2, 71.8, 76.8, 109.3, 123.6, 126.4, 128.1, 128.5, 128.7, 130.8, 131.0, 135.6, 139.0, 150.7 and 163.8; *m/z* (CI) 415 ($M^+ + NH_4$, 38%) and 340 (100).

(1*R*,5*S*,3*Z*)-5,6-Isopropylidenedioxy-1-phenylhex-3-enol 27

Sodium hydroxide (0.2 mol dm^{-3} in methanol; 10 cm^3) was added to a solution of nitrobenzoate **26** (0.54 g, 1.36 mmol) in dry methanol (2 cm^3) at ambient temperature and the mixture stirred for 18 h before being diluted with ethyl acetate, and washed with water and brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (3:1) as eluent, afforded the *title compound* **27** as a colourless oil (0.25 g, 73%) (Found: $M^+ + NH_4$, 266.1750. $C_{15}H_{24}NO_3$ requires *M*, 266.1756); $[\alpha]_D^{22}$ +48.9 (*c* 2.3, $CHCl_3$); ν_{max}/cm^{-1} 3448, 1216, 1156, 1057 and 860; δ_H 1.41 and 1.44 (each 3 H, s, CH_3CCH_3), 2.50 (1 H, br s, OH), 2.63 (2 H, m, 2-H_2), 3.50 and 3.98 (each 1 H, m, 6-H), 4.75 (2 H, m, 1-H and 5-H), 5.60 (1 H, m, 4-H), 5.73 (1 H, dt, *J* 10, 8, 3-H) and 7.38 (5 H, m, ArH); δ_C 25.9, 26.8, 37.5, 69.3, 71.9, 73.3, 109.2, 125.7, 127.6, 128.5, 130.1, 130.2 and 143.9; *m/z* (CI) 266 ($M^+ + NH_4$, 28%), 248 (M^+, 14), 231 (88) and 208 (100).

(2*S*,6*R*,3*Z*)-6-Phenylhex-3-ene-1,2,6-triol 28

Aqueous HCl (1 mol dm^{-3}; cm^3) was added dropwise to a solution of acetonide **27** (0.196 g, 0.79 mmol) in tetrahydrofuran (3 cm^3) at 0 °C. The solution was allowed to warm to ambient temperature and stirred for 18 h. Ethyl acetate (10 cm^3) was added to the mixture, the solution cooled to 0 °C and saturated aqueous $NaHCO_3$ (5 cm^3) added dropwise to it. The aqueous layer was extracted with ethyl acetate and the organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure to give the *title compound* **28** (0.155 g, 94%) which was used without further purification (Found: $M^+ + NH_4$, 226.1448. $C_{12}H_{20}NO_3$ requires *M*, 226.1443); $[\alpha]_D^{22}$ +99.6 (*c* 2.3, $CHCl_3$); ν_{max}/cm^{-1} 3347, 1494, 1028, 871 and 701; δ_H 2.65 (2 H, m, 5-H_2), 2.85 (3 H, br s, 3 × OH), 3.57 (2 H, m, 1-H_2), 4.49 (1 H, m, 2-H), 4.84 (1 H, t, *J* 6, 6-H), 5.60 (2 H, m, 3-H and 4-H) and 7.35 (5 H, m, ArH); δ_C 37.4, 66.1, 68.2, 73.0, 125.8, 127.7, 128.4, 129.3, 131.7 and 143.6; *m/z* (CI) 226 ($M^+ + NH_4$, 13%), 208 (M^+, 100) and 173 (45).

(1*R*,5*S*,3*Z*)-6-(*tert*-Butyldimethylsilyloxy)-1-phenylhex-3-ene-1,5-diol 21

tert-Butyldimethylsilyl chloride (70 mg, 0.46 mmol) was added dropwise to a solution of triol **28** (91 mg, 0.44 mmol), triethylamine (0.070 cm^3, 0.48 mmol) and a catalytic quantity of 4-dimethylaminopyridine in dichloromethane (2 cm^3) at 0 °C. The mixture was allowed to warm slowly to ambient temperature and stirred for 18 h, then partitioned between ethyl acetate (10 cm^3) and saturated aqueous $NaHCO_3$ (10 cm^3), and the aqueous phase extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate (3:1) as eluent, afforded the *title compound* **21** (94 mg, 67%) (Found: $M^+ + H$, 323.2038. $C_{18}H_{31}O_3Si$ requires *M*, 323.2042); $[\alpha]_D^{22}$ +86.3 (*c* 1.6, $CHCl_3$); ν_{max}/cm^{-1} 3385, 2858, 1256, 1110, 1053 and 837; δ_H 0.12 [6 H, s, $Si(CH_3)_2$], 0.86 [9 H, s, $SiC(CH_3)_3$], 2.69 (4 H, m, 2-H_2 and 2 × OH), 3.49 (1 H, dd, *J* 10, 8, 6-H), 3.61 (1 H, dd, *J* 10, 4, 6-H′), 4.47 (1 H, td, *J* 8, 4, 5-H), 4.84 (1 H, dd, *J* 6.5, 4.5, 1-H), 5.56 (1 H, dd, *J* 11, 8, 4-H), 5.66 (1 H, dt, *J* 11, 8, 3-H) and 7.35 (5 H, m, ArH); δ_C −5.3, −5.2, 18.4, 25.9, 37.7, 66.7, 68.2, 73.0, 125.8, 127.5, 128.4, 129.5, 131.2 and 144.0; *m/z* (CI) 340 ($M^+ + NH_4$, 12%), 323 ($M^+ + H$, 68), 322 (M^+, 57) and 305 (100).

(2*S*,6*S*,3*Z*)-Octa-3,7-diene-1,2,6-triol 32

Tetrabutylammonium fluoride (1 mol dm^{-3} in tetrahydrofuran; 4 cm^3) was added dropwise to a solution of diol **29** (0.87 g, 3.2 mmol) in tetrahydrofuran (20 cm^3) at 0 °C and the solution allowed to warm to ambient temperature and stirred for 18 h. Methanol (5 cm^3) and water (*ca.* 0.5 cm^3) were added to it and the mixture was stirred for 1 h before being concentrated under reduced pressure. Chromatography on silica gel using ethyl acetate as eluent, gave the *title compound* **32** (0.50 g, 99%) (Found: $M^+ + NH_4$, 176.1288. $C_8H_{18}NO_3$ requires *M*, 176.1287); $[\alpha]_D^{22}$ +13.5 (*c* 2.8, $CHCl_3$); ν_{max}/cm^{-1} 3381, 3016, 1645, 1426, 1075, 1026 and 734; δ_H 2.30 (1 H, dt, *J* 14, 4.5, 5-H), 2.49 (1 H, dt, *J* 14, 8, 5-H′), 3.58 (4 H, m, 1-H_2 and 2 × OH), 4.19 (2 H, m), 4.55 (1 H, m, 2-H), 5.17 (1 H, d, *J* 10.5, 8-H), 5.30 (1 H, d, *J* 17, 8-H′), 5.66 (2 H, m, 3-H and 4-H) and 5.93 (1 H, ddd, *J* 17, 10.5, 6, 7-H); δ_C 35.6, 66.0, 67.6, 71.6, 115.1, 130.0, 131.6 and 140.3; *m/z* (CI) 176 ($M^+ + NH_4$, 98%), 159 ($M^+ + H$, 53) and 158 (M^+, 100).

(2*S*,6*R*,3*Z*)-Oct-3-ene-1,2,6-triol 33

Following the procedure outlined for the synthesis of **32**, the diol **30** (90 mg, 0.33 mmol) gave the *title compound* **33** (45 mg, 86%) (Found: $M^+ + NH_4$, 178.1447. $C_8H_{20}NO_3$ requires *M*, 178.1443); $[\alpha]_D^{22}$ +28.3 (*c* 1.0, $CHCl_3$); ν_{max}/cm^{-1} 3346, 1659, 1461, 1076, 1022 and 869; δ_H 0.99 (3 H, t, *J* 7, 8-H_3), 1.55 (2 H, m, 7-H_2), 2.22 (1 H, m, 5-H), 2.38 (1 H, dt, *J* 14, 9, 5-H′), 3.60 (5 H, m, 1-H_2, 6-H and 2 × OH), 4.39 (1 H, br s, OH), 4.53 (1 H, m, 2-H) and 5.66 (2 H, m, 3-H and 4-H); δ_C 10.1, 30.2, 35.3, 66.1, 67.7, 72.0, 130.8 and 131.2; *m/z* (CI) 178 ($M^+ + NH_4$, 19%) and 160 (M^+, 100)

(3*R*,7*S*,5*Z*)-7,8-Isopropylidenedioxyoct-5-en-3-ol 34

Following the procedure outlined above for the synthesis of **25**, the triol **33** (0.081 g, 0.51 mmol) gave, after chromatography on silica gel using light petroleum–ethyl acetate (4:1) as eluent, the *title compound* **34** (0.076 g, 75%) (Found: $M^+ + NH_4$, 218.1754. $C_{11}H_{24}NO_3$ requires *M*, 218.1756); $[\alpha]_D^{22}$ +6.1 (*c* 1.5, $CHCl_3$); ν_{max}/cm^{-1} 3432, 1457, 1372, 1216, 1157, 1059 and 860; δ_H 1.00 (3 H, t, *J* 7.5, 1-H_3), 1.41 and 1.44 (each 3 H, s, CH_3CCH_3), 1.55 (2 H, m, 2-H_2), 1.90 (1 H, br s, OH), 2.33 (2 H, m, 4-H_2), 3.60 (2 H, m, 3-H and 8-H), 4.12 (1 H, dd, *J* 8, 6, 8-H′), 4.88 (1 H, q, *J* 7, 7-H), 5.64 (1 H, dd, *J* 11, 8, 6-H) and 5.76 (1 H, dt, *J* 11, 8, 5-H); δ_C 10.0, 25.9, 26.8, 29.8, 35.4, 69.4, 71.8, 72.3, 109.2, 130.1 and 131.2; *m/z* (CI) 218 ($M^+ + NH_4$, 43%), 201 ($M^+ + H$, 10) and 160 (100).

(3*R*,7*S*,5*Z*)-7,8-Isopropylidenedioxyoct-5-en-3-yl methanesulfonate 35

Methanesulfonyl chloride (0.11 cm^3, 1.43 mmol) was added dropwise to a solution of acetonide **34** (96 mg, 0.48 mmol) and triethylamine (0.2 cm^3, 1.43 mmol) in dichloromethane (2 cm^3) at 0 °C. The mixture was stirred at 0 °C for 1 h, then saturated

aqueous $NaHCO_3$ (2 cm^3) was added to it, and the mixture allowed to warm to ambient temperature before being partitioned between ethyl acetate (10 cm^3) and water (10 cm^3). The aqueous phase was extracted with ethyl acetate and the organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure to afford the *title compound* **35** (0.130 g, 97%) which was used without further purification (Found: $M^+ + NH_4$, 279.1259. $C_{12}H_{23}O_5S$ requires *M*, 279.1266); $[\alpha]_D^{22}$ +33.9 (*c* 1.5, $CHCl_3$); ν_{max}/cm^{-1} 1350, 1216, 1174, 1059, 911 and 859; δ_H 1.00 (3 H, t, *J* 7.5, 1-H_3), 1.38 and 1.41 (each 3 H, s, CH_3CCH_3), 1.73 (2 H, m, 2-H_2), 2.54 (2 H, m, 4-H_2), 3.01 (3 H, s, CH_3SO_3), 3.53 (1 H, t, *J* 8, 8-H), 4.09 (1 H, dd, *J* 8, 6, 8-H), 4.66 (1 H, quintet, *J* 6, 3-H), 4.80 (1 H, q, *J* 7, 7-H), 5.59 (1 H, dd, *J* 11, 7, 6-H) and 5.66 (1 H, dt, *J* 11, 6, 5-H); δ_C 9.5, 25.9, 26.8, 27.3, 32.4, 38.6, 69.3, 71.8, 83.7, 109.3, 127.9 and 131.2; *m/z* (CI) 296 ($M^+ + NH_4$, 10%), 279 ($M^+ + H$, 7) and 238 (100).

(2*S*,6*R*,3*Z*)-6-Methylsulfonyloxyoct-3-ene-1,2-diol 36

Following the procedure used to prepare **28**, the acetonide **35** (0.089 g, 0.32 mmol) was hydrolysed to give the *title compound* **36** (0.053 g, 70%); $[\alpha]_D^{22}$ +45.4 (*c* 1.5, $CHCl_3$); ν_{max}/cm^{-1} 3385, 1335, 1172, 1076, 976 and 911; δ_H 1.04 (3 H, t, *J* 7, 8-H_3), 1.79 (2 H, quintet, *J* 7, 7-H_2), 2.46 (1 H, dt, *J* 15, 5.5, 5-H), 2.66 (1 H, dt, *J* 15, 7, 5-H'), 3.05 (3 H, s, CH_3SO_3), 3.30–3.80 (4 H, m, 1-H_2 and 2 × OH), 4.59 (1 H, m, 2-H), 4.70 (1 H, m, 6-H) and 5.63 (2 H, m, 3-H and 4-H); δ_C 9.6, 27.6, 32.7, 38.8, 66.0, 68.3, 84.6, 127.4 and 132.3; *m/z* (CI) 256 ($M^+ + NH_4$, 53%), 238 (M^+, 15) and 160 (100).

(2*S*,6*S*,3*Z*)-1-(*tert*-Butyldimethylsilyloxy)-6-methylsulfonyloxyoct-3-en-2-ol 37

Following the procedure outlined for the synthesis of **21**, the diol **36** (0.156 g, 0.66 mmol) gave, after chromatography on silica gel using light petroleum–ethyl acetate (4:1) as eluent, the *title compound* **37** (0.168 g, 73%); $[\alpha]_D^{22}$ +51.6 (*c* 0.9, $CHCl_3$); ν_{max}/cm^{-1} 3446, 2858, 1338, 1174, 913 and 838; δ_H 0.12 [6 H, s, $Si(CH_3)_2$], 0.95 [9 H, s, $SiC(CH_3)_3$], 1.04 (3 H, t, *J* 7, 8-H_3), 1.79 (2 H, quintet, *J* 7, 7-H_2), 2.49 (1 H, dt, *J* 14, 5, 5-H), 2.66 (2 H, m, 5-H' and OH), 3.05 (3 H, s, CH_3SO_3), 3.49 (1 H, dd, *J* 10, 8, 1-H), 3.63 (1 H, dd, *J* 10, 4, 1-H'), 4.49 (1 H, m, 2-H), 4.72 (1 H, quintet, *J* 7, 6-H) and 5.62 (2 H, m, 3-H and 4-H); δ_C −5.4, −5.3, 9.5, 18.3, 25.9, 27.5, 32.7, 38.8, 66.6, 68.3, 84.1, 127.4 and 131.9; *m/z* (CI) 370 ($M^+ + NH_4$, 40%), 335 (21), 274 (100) and 257 (70).

(2*S*,6*S*,4*Z*)-7-(*tert*-Butyldimethylsilyloxy)hept-4-ene-1,2,6-triol 39

Diisobutylaluminium hydride (1 mol dm^{-3} in hexane; 2.44 cm^3) was added dropwise to a solution of the hydroxy ester **31** (0.176 g, 0.55 mmol) in dichloromethane (5 cm^3) at −78 °C. The solution was stirred for 1 h at −78 °C and then allowed to warm slowly to ambient temperature and stirred for 2 h. After cooling to −78 °C, methanol (2 cm^3) was added dropwise to it and the mixture allowed to warm to 0 °C. Saturated aqueous NH_4Cl (6 cm^3) was added to the mixture and the suspension was stirred for 18 h and then filtered through Celite. The filter cake was washed with ethyl acetate, and the filtrate was washed with 5% aqueous $NaSO_3$, dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography on silica gel using ethyl acetate as eluent, gave the *title compound* **39** (0.089 g, 65%) (Found: $M^+ + NH_4$, 294.2098. $C_{13}H_{32}NO_4Si$ requires *M*, 294.2101); ν_{max}/cm^{-1} 3362, 2858, 1255, 1100, 837 and 778; δ_H 0.12 [6 H, s, $Si(CH_3)_2$], 0.94 [9 H, s, $SiC(CH_3)_3$], 2.24 (1 H, m, 3-H), 2.48 (1 H, m, 3-H'), 3.40 (3 H, br s, 3 × OH), 3.56 (2 H, m), 3.66 (2 H, m), 3.77 (1 H, m, 2-H), 4.77 (1 H, td, *J* 7, 4, 6-H), 5.59 (1 H, dd, *J* 11, 8, 5-H) and 5.74 (1 H, m, 4-H); δ_C −5.4, −5.3, 18.4, 25.9, 32.0, 66.3, 66.6, 67.7, 70.9, 130.5 and 130.8; *m/z* (CI) 294 ($M^+ + NH_4$, 83%), 276 (M^+, 100) and 259 (75).

(2*S*,6*S*,4*Z*)-7-(*tert*-Butyldimethylsilyloxy)-2,6-dihydroxyhept-4-enyl toluene-*p*-sulfonate 41

Dibutyltin oxide (0.060 g, 0.24 mmol) was added to the triol **39** (0.067 g, 0.24 mmol) in methanol (6 cm^3) and the solution heated under reflux for 1 h and then cooled to 0 °C. Triethylamine (0.102 cm^3, 0.73 mmol) and toluene-*p*-sulfonyl chloride (0.140 g, 0.73 mmol) were added to it and the mixture was allowed to warm to ambient temperature and stirred for 18 h. The mixture was then filtered through Celite, the filter cake washed with ethyl acetate, and the filtrates were concentrated under reduced pressure. Chromatography on silica gel using light petroleum–ethyl acetate as eluent gave the *title compound* **41** (0.071 g, 68%) (Found: $M^+ + NH_4$, 448.2186. $C_{20}H_{38}NO_6SSi$ requires *M*, 448.2189); ν_{max}/cm^{-1} 3379, 2857, 1361, 1253, 1177, 1098 and 836; δ_H 0.12 [6 H, s, $Si(CH_3)_2$], 0.95 [9 H, s, $SiC(CH_3)_3$], 2.40 (2 H, m, 3-H_2), 2.48 (3 H, m, $ArCH_3$), 2.70 (2 H, br s, 2 × OH), 3.52 (1 H, dd, *J* 10, 8, 7-H), 3.65 (1 H, dd, *J* 10, 4, 7-H'), 3.88 (1 H, m, 2-H), 4.02 (2 H, m, 1-H_2), 4.42 (1 H, td, *J* 7, 3.5, 6-H), 5.62 (2 H, m, 4-H and 5-H) and 7.40 and 7.84 (each 2 H, d, *J* 7, ArH); δ_C −5.4, −5.3, 18.3, 21.7, 25.9, 31.9, 66.5, 67.7, 68.0, 128.9, 129.5, 130.0, 131.4, 132.7 and 145.0; *m/z* (CI) 448 ($M^+ + NH_4$, 100%) and 430 (M^+, 10).

Following the standard procedure outlined above, reaction of the aldehyde **47** (0.8 mmol) with stannane **18** which had been treated with tin(IV) chloride gave the toluene-*p*-sulfonate **41** (0.22 g, 71%).

2,3-Dihydroxypropyl toluene-*p*-sulfonate 45

A catalytic quantity of 4-dimethylaminopyridine and toluene-*p*-sulfonyl chloride (4.33 g, 22.7 mmol) were added to the 2,3-isopropylidenedioxypropanol **43** (2.0 g, 15.2 mmol) in pyridine (10 cm^3) at 0 °C and the solution was allowed to warm to ambient temperature and stirred for 18 h. The mixture was then decanted into a mixture of ice–water (100 cm^3) and ethyl acetate (100 cm^3), and allowed to warm to ambient temperature. The aqueous layer was extracted with ethyl acetate and the organic extracts were washed with saturated aqueous $CuSO_4$, brine and water, dried ($MgSO_4$) and then concentrated at reduced pressure to afford the toluene-*p*-sulfonate **44** (4.33 g, 100%) which was used without further purification; ν_{max}/cm^{-1} 1366, 1177, 1055, 979 and 828; δ_H 1.31 and 1.34 (each 3 H, s, CH_3CCH_3), 2.45 (3 H, s, CH_3Ar), 3.76 (1 H, dd, *J* 9, 5, 3-H), 4.05 (3 H, m, 1-H_2 and 3-H'), 4.28 (1 H, quintet, *J* 5, 2-H) and 7.35 and 7.79 (each 2 H, d, *J* 8, ArH); δ_C 22.2, 25.6, 27.1, 66.7, 70.0, 73.4, 110.5, 128.5, 130.4, 133.1 and 145.6; *m/z* (CI) 304 ($M^+ + NH_4$, 100%) and 287 ($M^+ + H$, 18).

Aqueous hydrogen chloride (3 mol dm^{-3}; 2 cm^3) was added to a solution of the toluene-*p*-sulfonate **44** (1.5 g, 5.2 mmol) in tetrahydrofuran (6 cm^3) at ambient temperature and the mixture stirred for 4 h. It was then cooled to 0 °C and saturated aqueous $NaHCO_3$ added dropwise to it until effervescence ceased. The mixture was extracted with ethyl acetate and the combined organic extracts were washed with brine, dried ($MgSO_4$) and then concentrated under reduced pressure to give the title compound **45**[21] (1.28 g, 99%) which was used without further purification; ν_{max}/cm^{-1} 3365, 1356, 1176, 1097, 1052 and 975; δ_H 2.41 (3 H, s, CH_3Ar), 3.3–3.95 (5 H, m, 3-H_2, 2-H and 2 × OH), 4.01 (2 H, m, 1-H_2), and 7.32 and 7.76 (each 2 H, d, *J* 8, ArH); δ_C 22.1, 63.3, 70.1, 71.3, 120.5, 130.5, 132.7 and 145.7; *m/z* (CI) 264 ($M^+ + NH_4$, 100%).

2-Oxoethyl toluene-*p*-sulfonate 47

Sodium periodate (6.75 g, 31.5 mmol) in water (60 cm^3) was added to a solution of the toluene-*p*-sulfonate **45** (5.16 g, 22.0 mmol) in dichloromethane (30 cm^3) at ambient temperature,

and the mixture stirred for 18 h. The organic phase was washed with water and brine and then heated under reflux over 4 Å molecular sieves for 3 h. The solution was decanted from the sieves, which were washed with dichloromethane, and the combined organic extracts were concentrated under reduced pressure to afford the *title compound* **47** (3.62 g, 77%); δ_H 2.47 (3 H, s, CH_3Ar), 4.51 (2 H, s, 2-H_2), 7.38 and 7.83 (each 2 H, d, *J* 8, ArH) and 9.62 (1 H, s, 1-H). This aldehyde was immediately dissolved in dichloromethane (34 cm^3) to give a solution of 0.5 mol dm^{-3} concentration which was used in subsequent reactions.

Acknowledgements

We thank Rhone Poulenc Rorer for a studentship (to R. J. M.) and Dr C. Smith of Rhone Poulenc Rorer for many helpful discussions.

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Paper 5/01888I
Received 24*th March* 1995
Accepted 26*th May* 1995