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USE OF 2-PHENYLSULPHONYL CYCLIC ETHERS IN THE PREPARATION OF TETRAHYDROPYRAN AND TETRAHYDROFURAN ACETALS AND IN SOME GLYCOSIDATION REACTIONS.

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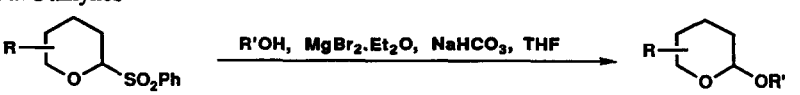
Abstract: *2-Phenylsulphonyl cyclic ethers undergo facile displacement of the sulphonyl group by alcohols, in the presence of magnesium bromide etherate and sodium bicarbonate in tetrahydrofuran, to give good yields of the corresponding acetals*

The preparation of tetrahydro-pyran and -furan ethers typically involves relatively acidic conditions[1] Since many functional groups may not be compatible with such acidity, we have examined the magnesium bromide induced displacement of the phenylsulphonyl moiety by alcohols under mildly basic conditions[2,3] (scheme) These mild conditions tolerate a wide variety of functional groups including furans, ketones, esters, silyl ethers, acetals, alkenes and alkynes



Scheme

The starting 2-phenylsuphonyl cyclic ethers **1-5**, were prepared in excellent yield, as previously reported, from lactols, lactol ethers, dihydro-pyrans, or -furans [4] Sulphone **6** was synthesised by oxidation of the corresponding sulphide with *meta*-chloroperbenzoic acid (*m*CPBA) In a typical experiment, these sulphones were converted into the corresponding acetals by stirring in tetrahydrofuran (THF) with the required alcohol, magnesium bromide etherate and sodium bicarbonate, at room temperature overnight (Tables 1-4)

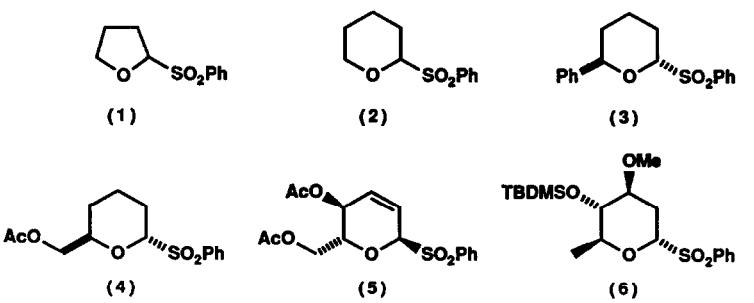
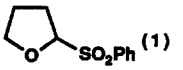
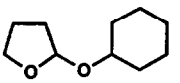
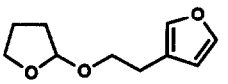
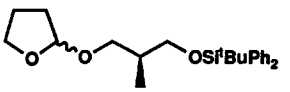
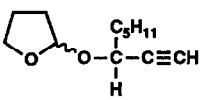
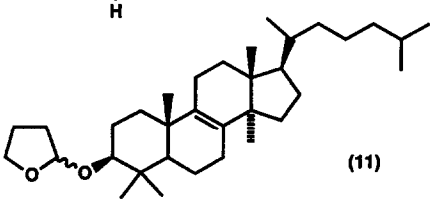


TABLE 1

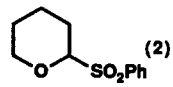
PRODUCTS OF REACTIONS OF ALCOHOLS WITH  (1)

ENTRY	PRODUCT		YIELD	CONDITIONS
1		(7)	98 %	Method A
2		(8)	84 %	Method B
3		(9)	Quant	Method A
4		(10)	99 %	Method A
5		(11)	89 %	Method A

CONDITIONS for Tables1-3
Method A· 1 eq sulphone, 2 eq alcohol, 2 eq $MgBr_2$ Et_2O, 1 eq $NaHCO_3$, stirred overnight at room temperature
Method B 1 eq sulphone, 1 eq. alcohol, 2 eq $MgBr_2$ Et_2O, 1 eq $NaHCO_3$, stirred overnight at room temperature

From the tables it can be seen that relatively hindered tertiary alcohols may be used (Table 2, entry 2 and Table 3, entry 2) [5] Phenols will also react, although the yields have been less than 50% in the few examples investigated (Table 2, entry 13 and Table 3, entry 6). In all situations where the pyran ring additionally carries a substituent in the C-6 position (Table 3), one observes preferential *trans*-stereoselectivity in the formation of the acetal product, although the ratio of products depends on the steric bulk of the incoming group This is in contrast to our work on the substitution of the phenylsulphonyl group by carbon nucleophiles, where the 2,6-*trans*-isomer is usually the only product, suggesting preferred axial attack by the incoming nucleophile at the anomeric centre[4] Our reasoning is that, with the oxygen nucleophiles, equilibration to the thermodynamic mixture of products is possible, and thus a stereochemical mixture is obtained In some cases, as shown in Table 4, glycosidations can be acheived, using carbohydrate derivatives as either the sulphone or alcohol component, with varying degrees of success [6,7] In examples where the reaction was slow, considerable rate enhancement could be acheived by the use of ultrasonication in a small cleaning bath[8], or even warming to gentle reflux

TABLE 2

PRODUCTS OF REACTIONS OF ALCOHOLS WITH  **(2)**

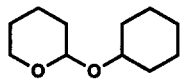
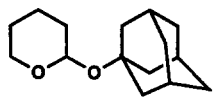
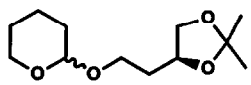
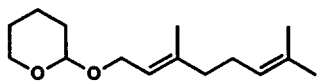
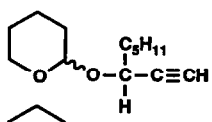
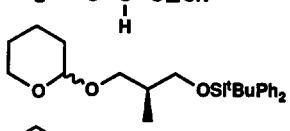
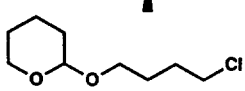
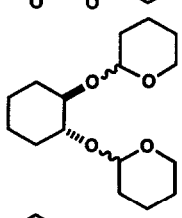
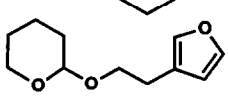
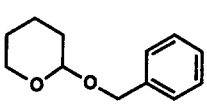
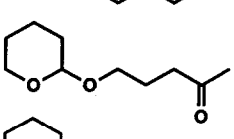
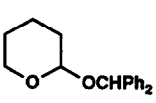
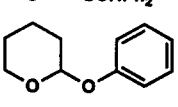
ENTRY	PRODUCT		YIELD	CONDITIONS
1		(12)	92 %	Method A
2		(13)	80 %	Method A
3		(14)	78 %	Method A
4		(15)	90 %	Method B
5		(16)	96 %	Method A
6		(17)	Quant.	Method A
7		(18)	97 %	Method A
8		(19)	67 %	Method B
9		(20)	67 %	Method B
10		(21)	95 %	Method B
11		(22)	84 %	Method A
12		(23)	67 %	Method A
13		(24)	47 %	Method B

TABLE 3

PRODUCTS OF REACTION OF ALCOHOLS WITH 6-SUBSTITUTED TETRAHYDROPYRANYLSULPHONES

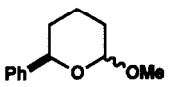
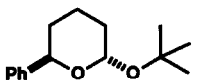
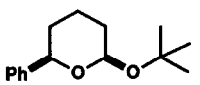
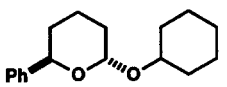
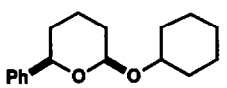
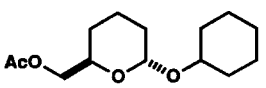
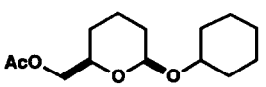
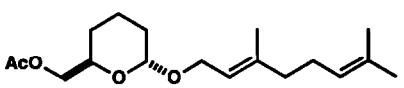
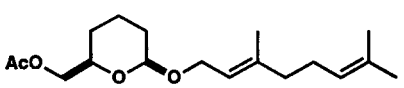
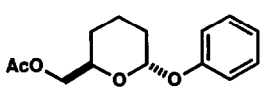
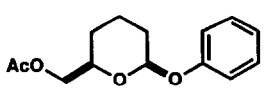
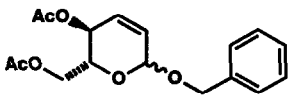
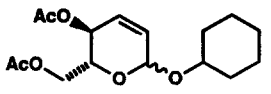
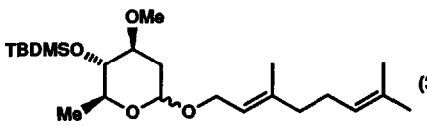
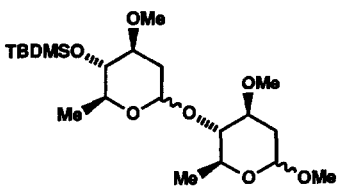
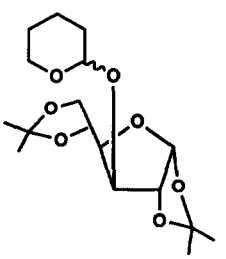
ENTRY	PRODUCT		YIELD	CONDITIONS
1		(25)	70 % trans:cis 80:20	Method A with sonication
2		(26)	40 %	Method B
		(27)	38 %	
3		(28)	62 %	Method B with sonication
		(29)	11 %	
4		(30)	58 %	Method B Four days room temp
		(31)	18 %	
5		(32)	59 %	Method B Four days room temp
		(33)	26 %	
6		(34)	39 %	Method B
		(35)	11 %	

TABLE 4

GLYCOSIDATION REACTIONS

ENTRY	PRODUCT		YIELD	CONDITIONS
1		(36)	70 % eq ax 22.78	Method A with sonication
2		(37)	76 % eq·ax 13 87	Method B with sonication
3		(38)	58 % eq:ax 33:67	Method A at reflux
4		(39)	65 % major prpduct is αα	Method A with sonication
5		(40)	53 %	Method B with sonication

CONDITIONS
Method A: 1 eq. sulphone, 5 eq alcohol, 2 eq $MgBr_2.Et_2O$, 1 eq $NaHCO_3$.
Method B: 1 eq. sulphone, 1 eq. alcohol, 2 eq. $MgBr_2.Et_2O$, 1 eq $NaHCO_3$, stirred overnight at room temperature

In summary, the above method constitutes a new, mild, room temperature procedure for the formation of tetrahydropyran and tetrahydrofuran acetals, with the considerable advantage of being weakly basic rather, than acidic The commercial availability of the tetrahydropyranyl sulphone (2), also increases its appeal as a protecting group reagent for alcohols

Acknowledgements: *We thank the SERC and SmithKline Beecham Pharmaceuticals, Harlow, Essex for a CASE Award (S V), the SERC for an Instant Award (D S.B), and Schering Agrochemicals Ltd , Saffron Walden, Essex for additional financial support (D.S.B)*

Experimental:

Solutions were dried over anhydrous sodium sulphate or anhydrous magnesium sulphate, and solvents by standard methods [9] The products were purified by column chromatography on Merck silica gel 60 (Art. 9385 230-400 mesh) under pressure using diethyl ether / petrol as the solvent unless otherwise stated. "Petrol" refers to the fraction boiling at 40-60°C Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer as liquid films or chloroform solutions ^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker WM-250, Jeol GSX-270 or Bruker AM-500 spectrometers Mass spectra were recorded on a VG Micromass 7070B instrument, except for the accurate mass measurements, for which we thank the S E.R C Mass Spectrometry Service at the University of Swansea Microanalyses were performed by the analytical department of Imperial College

The **Sulphones (1)-(5)** were prepared as previously published[4]

4-*O*-(*tert*-Butyldimethylsilyl)-1-deoxy-1-(phenylsulphonyl)-α-L-oleandrose (6).- Phenyl 4-*O*-(*tert*-butyldimethylsilyl)-1 deoxy-1-thio-α-L-oleandroside[10] (333mg, 0 90 mmol) was dissolved in dichloromethane (20 ml) at 0°C and treated with *meta*-chloroperbenzoic acid (0.51g, 85%, 2.51 mmol, 2 8 equiv) in the presence of saturated aqueous sodium hydrogen carbonate solution (20 ml) The reaction was stirred overnight at room temperature Work-up and purification by silica gel chromatography (gradient elution, Et_2O petrol, 1 3-2 3) gave the sulphone **6** as a white solid (285 mg, 0 71 mmol, 79%), m p 54-58°C, $[\alpha]_D^{20}$ -116 8° (c 1 02 in $CHCl_3$), ν_{max} (film) 3063, 2930, 2890, 2855, 1460, 1446, 1387, 1308, 1289, 1249, 1206, 1141, 1124, 1081, 1059, 888, 837, 777, 730, 687 and 665 cm^{-1}, δ_H (500 MHz) 0 06 (3H, s, $SiCH_3$), 0 09 (3H, s, $SiCH_3$), 0 88 (9H, s, $SiC(CH_3)_3$), 1 15 (3H, d, *J* 6 5 Hz, 6-CH_3), 1 92 (1H, ddd,*J* 14 5 9 5 7 0 Hz, 2-Hax), 2 93 (1H, ddd,*J* 14 5 5 0 3 0 Hz, 2-Heq), 3 18 (1H, dd, *J* 9 0 7 5 Hz, 4-H), 3 40 (3H, s, 3-OCH_3), 3 72 (1H, ddd, *J* 9 5 7 0 5 0 Hz, 3-H), 4 24 (1H, dq, *J* 9 0 6 5 Hz, 5-H), 4 75 (1H, dd, *J* 7 0 3 0 Hz, 1-H), 7 56-7 59 (2H, m) 7 65-7 69 (1H, m) and 7 89-7 91 (2H, m) (PhH), m/z 343 $(M\text{-}^tBu)^+$, 311 $(M\text{-}^tBu\text{-}CH_4O)^+$ 259 $(M\text{-}PhSO_2)^+$, 243 $(M\text{-}PhSO_2H\text{-}CH_3)^+$, 227 $(M\text{-}PhSO_2\text{-}CH_4O)^+$, 201 $(M\text{-}PhSO_2H\text{-}^tBu)^+$, 115 $(^tBuMe_2Si)^+$, 89 $(C_4H_9O_2)^+$, 73 $(C_3H_5O_2)^+$, and 59 $(C_3H_7O)^+$. (Observed $(M\text{-}^tBu)^+$, 343 1035, calc for $C_{15}H_{23}O_5SSi$ $(M\text{-}^tBu)$, 343 103). (Found C, 57 01, H, 8 10, $C_{19}H_{32}O_5SSi$ requires C , 56 97, H, 8 05%)

General Method for 2-Substitution of Cyclic Ethers by Alcohols.- A mixture of the sulphone (1 equiv), alcohol (1-2 equiv), magnesium bromide etherate (2 equiv) and sodium hydrogen carbonate (1 equiv) in dry, freshly distilled THF (5 ml/mmol) was stirred at room temperature for 15-24 hours under argon The reaction mixture was quenched with 1N NaOH and extracted with ether The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo* Products were purified by silica gel chromatography (eluted with Et_2O petrol, 1 15 unless stated otherwise)

2-(Cyclohexyloxy)tetrahydrofuran (7)[1g].- Reaction of tetrahydro-2-(phenylsulphonyl)furan (1) (208 mg, 0 98 mmol) with cyclohexanol (0 210 ml, 200 mg, 2 0 mmol, 2 0 equiv), $MgBr_2.Et_2O$ (521 mg, 2 0 mmol, 2 1 equiv) and $NaHCO_3$ (86 mg, 1 0 mmol, 1 0 equiv), followed by standard work-up and chromatography, gave the acetal product **7** (164 mg, 0 96 mmol, 98%) as a colourless oil, ν_{max} (film) 2922, 2850, 1726, 1459, 1259, 1068 and 1023 cm^{-1}, δ_H (250 MHz) 1 00-2 10 (14H, m, 3-H_2 4-H_2 2'-H_2 3'-H_2 4'-H_2 5'-H_2 6'-H_2), 3 50 (1H, tt, *J* 9 5 4 5 Hz, 1'-H), 3 77-3 95 (2H, m, 5-H_2), 5 27 (1H, dd, *J* 4 5 1 5 Hz, 2-H), m/z 170 $(M)^+$, 141 $(M\text{-}C_2H_5)^+$, 125 $(M\text{-}C_2H_5O)^+$, 96 $(C_6H_8O)^+$, 84 $(C_6H_{14})^+$ and 71 $(C_4H_7O)^+$, (Observed $(M+NH_4)^+$, 188 1650, calc for $C_{10}H_{22}NO_2$ $(M+NH_4)$, 188 1650)

2-[2-(3-Furyl)ethyloxy]tetrahydrofuran (8).- Reaction of tetrahydro-2-(phenylsulphonyl)furan (1) (232 mg, 1 1 mmol) with 2-(3-furyl)ethanol (110 mg, 0 98 mmol, 1 0 equiv), $MgBr_2$ Et_2O (525 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (95 mg, 1 1 mmol, 1 0 equiv), followed by standard work-up and chromatography (Et_2O petrol, 1 10), gave the acetal product **8** (167 mg, 0 92

mmol, 84%) as a colourless oil, ν_{max} (film) 3131, 2947, 2914, 2879, 1456, 1348, 1324, 1184, 1160, 1122, 1094, 1067, 1039, 979, 920, 873, 781 and 727 cm^{-1}, δ_H (250 MHz) 1 75-2 07 (4H, m, 3-H_2 4-H_2), 2 68 (2H, t, *J* 6 5 Hz, 2'-H_2), 3 55 (1H, dt, *J* 9 5 7 0 Hz, 5-H), 3 72-3 89 (3H, m, 5-H, 1'-H_2), 5 13 (1H, dd, *J* 3 5 2 0 Hz, 2-H), 6 30 (1H, br s, 4"-H), 7 27 (1H, s, 2"-H), 7 34 (1H, br s, 5"-H), m/z 182 $(M)^+$, 123 $(M-C_3H_7O)^+$, 112 $(M-C_4H_6O)^+$, and 71 $(C_4H_7O)^+$, (Observed M^+, 182 0943, $C_{10}H_{14}O_3$ M requires 182 0943)

[2*RS*(*S*)]-2-[3-(*tert*-Butyldiphenylsilyloxy)-2-methylpropyloxy]tetrahydrofuran (9).- Reaction of tetrahydro-2-(phenylsulphonyl)furan (**1**) (215 mg, 1 0 mmol) with (2*S*)-(3-*tert*-butyldiphenylsilyloxy)-2-methylpropanol (660 mg, 2 0 mmol, 2 0 equiv), $MgBr_2$ Et_2O (516 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (92 mg, 1 1 mmol, 1 1 equiv), followed by standard work-up and chromatography (Et_2O petrol, 1 9), gave the acetal product **9** (398 mg, 1 0 mmol, Quant.) as a colourless oil and an inseparable mixture of diastereoisomers at C-2 (*ca* 1 1), ν_{max} (film) 3068, 3047, 2955, 2929, 1740, 1470, 1426, 1388, 1359, 1233, 1186, 1111, 1040, 998, 971, 931, 920, 823, 740, 703 and 614 cm^{-1}, δ_H (250 MHz) 0 97 (3H, d, *J* 6 5 Hz, 2'-CH_3), 1 05 (9H, s, $(CH_3)_3$), 1 75-2 05 (5H, m, 3-H_2 4-H_2 2'-H_2), 3 33 (0 5H, dd, *J* 10 5 6 0 Hz, 3'-H one isomer), 3 44 (0 5H, dd, *J* 9 5 7 0 Hz, 3'-H one isomer), 3 51-3 66 (2 5H, m, 1'-H, 1'-H one isomer, 3'-H), 3 68 (0 5H, dd, *J* 9 5 6 5 Hz, 1'-H one isomer), 3 79-3 87 (2-H, m, 5-H_2), 5 08 (1H, t, *J* 2 0 Hz, 2-H), 7 35-7 47 (6H, m) and 7 62-7 71 (4H, m) (PhH), m/z 341 $(M-{}^tBu)^+$, 327 $(M-C_4H_7O)^+$, 211 $(M+H-{}^tBu-C_4H_7O)^+$, and 71 $(C_4H_7O)^+$, (Observed $(M+H)^+$, 399.2355, calc for $C_{24}H_{35}O_3Si$ (M+H), 399 2355)

2-(1-Ethynylhexyloxy)tetrahydrofuran (10).- Reaction of tetrahydro-2-(phenylsulphonyl)furan (**1**) (202 mg, 0 95 mmol) with oct-1-yn-3-ol (0 30 ml, 258 mg, 2 0 mmol, 2 1 equiv), $MgBr_2$ Et_2O (522 mg, 2 0 mmol, 2 1 equiv) and $NaHCO_3$ (93 mg, 1 1 mmol, 1 2 equiv), followed by standard work-up and chromatography, gave the acetal product **10** as a separable mixture of diastereoisomers (*ca* 1 1) (total yield, 185 mg, 0 94 mmol, 99%) both colourless oils Diastereoisomer of higher Rf ν_{max} (film) 3309, 2921, 2850, 1707, 1459, 1377, 1260 and 1017 cm^{-1}, δ_H (250 MHz) 0 88 (3H, t, *J* 7 0 Hz, 6'-H_3), 1 25-1 50 (6H, m, 3'-H_2 4'-H_2 5'-H_2) 1 60-1 75 (2H, m, 4-H_2) 1 78-2 05 (4H, m, 3-H_2 2'-H_2), 2 38 (1H, d, *J* 2 0 Hz, C≡CH), 3 81-3 89 (2H, m, 5-H_2), 4 33 (1H, td, *J* 6 5 2 0 Hz, 1'-H), 5 46 (1H, dd, *J* 3 5 1 5 Hz, 2-H), m/z 196 (M), 195 $(M-H)^+$, 167 $(M-C_2H_5)^+$, 153 $(M-C_3H_7^+)$, 125 $(C_8H_{13}O)^+$, 109 $(C_8H_{13})^+$, and 71 $(C_4H_7O)^+$ or $(C_5H_{11})^+$, (Observed $(M+NH_4)^+$, 214 1815, calc for $C_{12}H_{24}NO_2$ $(M+NH_4)$, 214 1807) Diastereoisomer of lower Rf ν_{max} (film) 3306, 2930, 2859, 1459, 1378, 1326, 1185, 1115, 1086, 1030 and 920 cm^{-1}, δ_H (250 MHz) 0 89 (3H, t, *J* 7 0 Hz, 6'-H_3), 1 20-1 50 (6H,m, 3'-H_2 4'-H_2 5'-H_2) 1 62-1 78 (2H, m, 4-H_2) 1 78-1 98 (3H, m, 3-H 2'-H_2), 1 98-2 10 (1H, m, 3-H), 2 42 (1H, d, *J* 2 0 Hz, C≡CH), 3 89 (1H, td, *J* 8 0 6 0 Hz, 5-H), 4 01 (1H, td, *J* 8 0 6 0 Hz, 5-H), 4 22 (1H, td, *J* 6 5 2 0 Hz, 1'-H), 5 28 (1H, t, *J* 2 5 Hz, 2-H), m/z 195 $(M-H)^+$, 153 $(M-C_3H_7)^+$, 125 $(C_8H_{13}O)^+$, and 71 $(C_4H_7O)^+$ or $(C_5H_{11})^+$, (Observed $(M+NH_4)^+$, 214 1807, calc for $C_{12}H_{24}NO_2$ $(M+NH_4)$, 214 1807)

Tetrahydro-2-(lanost-8-en-3-yloxy)furan (11).- Reaction of tetrahydro-2-(phenylsulphonyl)furan (**1**) (156 mg, 0 74 mmol, 1 5 equiv) with lanost-8-en-3-ol (215 mg, 0 50 mmol, 1 0 equiv), $MgBr_2$ Et_2O (260 mg, 1 0 mmol, 2 0 equiv) and $NaHCO_3$ (43 mg, 0 50 mmol, 1 0 equiv), followed by standard work-up and chromatography, gave the acetal product **11** (222 mg, 0 45 mmol, 89%) as a white solid, (m p 96-98°C) and an inseparable mixture of diastereoisomers at C-2 (*ca* 2 3), ν_{max} (film) 2944, 2014, 1463, 1369 and 1031 cm^{-1}, δ_H (250 MHz) 0 50-2 10 (54H, m, 3-H_2 4-H_2 and all protons of steroid except 3'-H), 3 06 (0 4H, dd, *J* 14 0 5 0 Hz, 3'-H one isomer), 3 22 (0 6H, dd, *J* 13 5 5 0 Hz, 3'-H one isomer), 3 76-3 97 (2H, m, 5-H_2), 5 17 (0 4H, t, *J* 3 5 Hz, 2-H one isomer), 5 27 (0 6H, dd, *J* 4 5 2 0 Hz, 2-H one isomer), m/z 498 $(M)^+$, 483 $(M-CH_3)^+$, 428 $(M-C_4H_6O)^+$, 413 $(M-C_5H_9O)^+$, 395 $(M-C_5H_9O_2)^+$ and 71 $(C_4H_7O)^+$, (Observed M^+, 498 4437, calc for $C_{34}H_{58}O_2$ M, 498 4437), (Found C, 81 99, H, 11 85, $C_{34}H_{58}O_2$ requires C, 81 87, H, 11 72%)

2-(Cyclohexyloxy)tetrahydro-2*H*-pyran (12)[1a].- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (**2**) (230 mg, 1 0 mmol) with cyclohexanol (0 22 ml, 222 mg, 2 2 mmol, 2 2 equiv), $MgBr_2$ Et_2O (513 mg, 2 0 mmol, 1 9 equiv) and $NaHCO_3$ (87 mg, 1 0 mmol, 1 0 equiv), followed by standard work-up and chromatography, gave the acetal product **12** (173 mg, 0 94 mmol, 92%) as a colourless oil, ν_{max} (film) 2932, 2855, 1449, 1356, 1201, 1169, 1117, 1063, 1022, and 998 cm^{-1}, δ_H (250 MHz) 1 10-2 00 (16H, m, 3-H_2 4-H_2 5-H_2 2'-H_2 3'-H_2 4'-H_2 5'-H_2 6'-H_2), 3 43-3 52 (1H, m, 6-H), 3 59 (1H, tt, *J* 9 5 4 0 Hz, 1'-H), 3 87-3 95 (1H, m, 6-H), 4 70 (1H, dd, *J* 4 5 3 0 Hz, 2-H), m/z 102 $(C_5H_{10}O_2)^+$, and 85 $(C_5H_9O)^+$, (Found C, 71 79, H, 11 14, calc for $C_{11}H_{20}O_2$, C, 71 70, H, 10 94%)

2-(Tricyclo[3.3.1.1^{3,7}]dec-1-yloxy)tetrahydro-2*H*-pyran (13)[1c].- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (230 mg, 1 0 mmol) with adamantanol (302 mg, 2 0 mmol, 2 0 equiv), $MgBr_2.Et_2O$ (515 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (95 mg, 1 1 mmol, 1 1 equiv), followed by standard work-up and chromatography, gave the acetal product 13 (193 mg, 0 82 mmol 80%) as a colourless oil, ν_{max} (film) 2906, 2849, 1446, 1353, 1305, 1200, 1185, 1132, 1118, 1102, 1075, 1041, 1023, 998 and 982 cm^{-1}, δ_H (250 MHz) 1 43-1 58 (4H, m, 4-H_2 5-H_2), 1 63 (6H, t, *J* 3 5 Hz, 3 x γ-H_2), 1 65-1 93 (8H, m, 3-H_2 3 x α-H_2), 2 12 (3H, br s, 3 x β-H), 3 44 (1H, ddd, *J* 11 5 6 0 4 5 Hz, 6-Hax), 3 95 (1H, dt, *J* 11 0 4 0 Hz, 6-Heq), 4 83 (1H, dd, *J* 6 0 4 0 Hz, 2-H), m/z 236 (M)$^+$, 218 (M-H_2O)$^+$, 190 (M-H_2O-C_2H_4)$^+$, 152 ($C_{10}H_{16}O$)$^+$, 135 ($C_{10}H_{15}$)$^+$ and 85 (C_5H_9O)$^+$, (Observed M$^+$, 236 1776, calc for $C_{15}H_{24}O_2$ M, 236 1776)

[4*S*(*RS*)]-4-[2-(Tetrahydro-2*H*-pyran-2-yloxy)ethyl]-2,2-dimethyl-1,3-dioxolane (14).- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (226 mg, 1 0 mmol) with (*S*)-2,2-dimethyl-1,3-dioxolane-4-ethanol (310 mg, 2 1 mmol, 2 1 equiv), $MgBr_2$ Et_2O (526 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (88 mg, 1 1 mmol, 1 1 equiv), followed by standard work-up and chromatography, gave the acetal product 14 (179 mg, 0 78 mmol 78%) as a colourless oil and an inseparable mixture of diastereoisomers at C-2' (*ca* 1 1), ν_{max} (film) 2982, 2939, 2870, 1451, 1440, 1377, 1366, 1352, 1322, 1250, 1201, 1161, 1138, 1123, 1076, 1036, 1023, 989, 908, 866 and 814 cm^{-1}, δ_H (250 MHz) 1 35 and 1 39 (2 x 3H, 2 x s, $CH(CH_3)_2$), 1 40-2 00 (8H, m, 3"-H_2 4"-H_2 5"-H_2 1'-H_2), 3 39-3 61 (3H, m, 6"-H 2'-H 5-H), 3 75-3 98 (2H, m, 6"-H 5-H), 4 06 (1H dt, *J* 8 0 6 0 Hz, 2'-H), 4 12-4 25 (1H, m, 4-H), 4 55 and 4 57 (2 x 0 5H, 2 x t, *J* 3 0 Hz, 2"-H), m/z 229 (M-H)$^+$, 215 (M-CH_3)$^+$, 172 (M-C_3H_6O)$^+$, 159 (M-C_4H_7O)$^+$, 145 (M-C_5H_9O)$^+$, 129 (M-$C_5H_9O_2$)$^+$ or ($C_5H_9O_2CH_2CH_2$)$^+$, 115 ($C_5H_9O_2CH_2$)$^+$, 101 ($C_5H_9O_2$)$^+$, and 85 (C_5H_9O)$^+$, (Observed (M+NH_4)$^+$, 248 1862, calc for $C_{12}H_{26}NO_4$ (M+NH_4), 248 1862)

(*E*)2-(3,7-Dimethyl-2,6-octadienyloxy)tetrahydro-2*H*-pyran (15)[1c].- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (228 mg, 1 0 mmol) with geraniol (0 175 ml, 156 mg, 1 0 mmol, 1 0 equiv), $MgBr_2.Et_2O$ (521 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (88 mg, 1 1 mmol, 1 0 equiv), followed by standard work-up and chromatography, gave the acetal product 15 (217 mg, 0 91 mmol, 90%) as a colourless oil, ν_{max} (film) 2939, 1440, 1376, 1200, 1117, 1077, and 1023 cm^{-1}, δ_H (250 MHz) 1 42-2 15 (10H, m, 3-H_2 4-H_2 5-H_2 4'-H_2 5'-H_2), 1 59 (3H, s, 3'-Me), 1 65 (6H, s, 7'-Me), 3 45-3 54 (1H, m, 6-H), 3 84-3 93 (1H, m, 6-H), 4 02 (1H, dd, *J* 11 5 7 5 Hz, 1'-H), 4 23 (1H, ddd, *J* 12 0 6 5 0 5 Hz, 1'-H), 4 62 (1H, t, *J* 3 5 Hz, 2-H), 5 08 (1H, tt, *J* 4 0 1 5 Hz, 6'-H), 5 35 (1H, tt, *J* 6 5 1 0 Hz, 2'-H), m/z 238 (M)$^+$, 195 (M-C_2H_3O)$^+$, 85 (C_5H_9O)$^+$ and 69 (C_5H_9)$^+$, (Observed M$^+$, 238 1933, calc for $C_{15}H_{24}O_2$ M, 238 1933), (Found C, 75 47, H, 11 17, calc for $C_{15}H_{26}O_2$, C, 75 58, H, 10 99%)

2-(1-Ethynylhexyloxy)tetrahydro-2*H*-pyran (16).- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (229 mg, 1 0 mmol) with oct-1-yn-3-ol (0 30 ml, 259 mg, 2 1 mmol, 2 0 equiv), $MgBr_2$ Et_2O (518 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (84 mg, 1 0 mmol, 1 0 equiv), followed by standard work-up and chromatography, gave the acetal product **16** as a separable mixture of diastereoisomers (*ca* 1 1) (total yield, 205 mg, 0 97 mmol, 96%), both colourless oils Diastereoisomer of higher Rf ν_{max} (film) 3306, 2939, 2867, 1465, 1440, 1377, 1353, 1259, 1201, 1183, 1158, 1126, 1115, 1077, 1037, 1022, 980, 907, 870, 815, 656 and 624 cm^{-1}, δ_H (250 MHz) 0 90 (3H, t, *J* 7 0 Hz, 8'-H_3), 1 20-1 40 (4H, m) 1 40-1 67 (6H, m) 1 67-1 88 (4H, m) (3-H_2 4-H_2 5-H_2 2'-H_2 3'-H_2 4'-H_2 5'-H_2), 2 37 (1H, d, *J* 2 5 Hz, C≡CH), 3 52 (1H, ddd, *J* 11 0 6 0, 5 0 Hz, 6-H), 3 80 (1H, ddd, *J* 11 5 8 0 3 5 Hz, 6-H), 4 40 (1H, td, *J* 6 5 2 0 Hz, 1'-H), 4 67 (1H, t, *J* 3 0 Hz, 2-H), m/z 209 (M-H)$^+$, 181 (M-C_2H_5)$^+$, 139 (M-C_5H_{11})$^+$, 109 (C_8H_{13})$^+$, 101 ($C_5H_9O_2$)$^+$, 85 (C_5H_9O)$^+$ and 67 (C_5H_7)$^+$, (Observed (M+NH_4)$^+$, 228 1964, calc for $C_{13}H_{26}NO_2$ (M+NH_4), 228 1963) Diastereoisomer of lower Rf ν_{max} (film) 3306, 2941, 2859, 1465, 1452, 1440, 1379, 1351, 1334, 1320, 1260, 1201, 1184, 1117, 1078, 1051, 1023, 981, 910, 870, 816, 652 and 623 cm^{-1}, δ_H (500 MHz) 0 89 (3H, t, *J* 7 5 Hz, 6'-H_3), 1 27-1 47 (4H, m) 1 40-1 50 (2H, m) 1 50-1 65 (4H, m) 1 65-1 78 (3H, m) 1 80-1 90 (1H, m) (3-H_2 4-H_2 5-H_2 2'-H_2 3'-H_2 4'-H_2 5'-H_2), 2 43 (1H, d, *J* 1 5 Hz, C≡CH), 3 53 (1H, ddd, *J* 11 5 4 5 1 0 Hz, 6-Heq), 4 01 (1H, ddd, *J* 11 5 9 0, 3 0 Hz, 6-Hax), 4 27 (1H, td, *J* 6 5 2 0 Hz, 1'-H), 4 74 (1H, t, *J* 3 5 Hz, 2-H), m/z 209 (M-H)$^+$, 181 (M-C_2H_5)$^+$, 167 (M-C_2H_3O)$^+$, 139 (M-C_5H_{11})$^+$, 109 (C_8H_{13})$^+$, 101 ($C_5H_9O_2$)$^+$, 85 (C_5H_9O)$^+$ and 67 (C_5H_7)$^+$, (Observed M$^+$, 210 1620, calc for $C_{13}H_{22}O_2$ M, 210 1620)

[2*RS*(*S*)]-2-[3-(*tert*-Butyldiphenylsilyloxy)-2-methylpropyloxy]tetrahydro-2*H*-pyran (17).- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (225 mg, 0 99 mmol) with (2*S*)-3-(*tert*-butyldiphenylsilyloxy)-2-methylpropanol (660 mg, 2 0 mmol, 2 0 equiv), $MgBr_2$ Et_2O (514 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (96 mg, 1 2 mmol, 1 2 equiv), followed by standard work-up and chromatography, gave the acetal product 17 (410 mg, 0 99 mmol, Quant.) as a colourless oil and an inseparable mixture of diastereoisomers (*ca* 1 1), ν_{max} (film) 3068, 3047, 2931, 2807, 1740, 1588, 1468, 1426, 1387, 1359, 1260, 1200, 1184, 1169, 1112, 1078, 1060, 1033, 976, 903, 869, 823, 740, 703 and 614 cm^{-1}, δ_H (500 MHz) 0 98 and 1 00 (3H, 2 x d, *J* 7 5 Hz, 2'-CH_3), 1 05 (9H, s, $(CH_3)_3$), 1 46-1 62 (4H, m, 4-H_2 5-H_2), 1 64-1 71, (1H, m, 3-Hax), 1 75-1 85, (1H, m, 3-Heq), 1 95-2 05, (1H, m, 2'-H), 3 35 (0 5H, dd, *J* 9 5 5 5 Hz, 3'-H one isomer), 3 45 (0 5H, dd, *J* 9 5 7 0 Hz, 3' one isomer), 3 46-3 60 (1H, m, 6-Heq), 3 60-3.68 (2 5H, m, 3'-H 1'-*H* one isomer 1'-H), 3 77 (0 5H, dd, *J* 9 5 6 5 Hz, 1'-H one isomer), 3 83 (0 5H, ddd, *J* 11 5 8 5 3 0 Hz, 6-Hax one isomer), 3 86 (0 5H, ddd, *J* 11.5 8 5 3 0 Hz, 6-Hax one isomer), 4 57 (1H, dd, *J* 8 5 2 0 Hz, 2-H), 7 33-7.45 (6H, m) and 7 54-7 6 (4H, m) (PhH), m/z 313 $(M-C_5H_9OCH_2)^+$, 271 $(M+H-{}^tBu-C_5H_9O)^+$, 241 $(M+H-{}^tBu-C_5H_9O_2CH_2)^+$, 227 $(CH_3CH_2OSiPh_2)^+$, 199 $(Ph_2SiOH)^+$, 85 $(C_5H_9O)^+$ and 69 $(C_5H_9)^+$, (Observed $(M+NH_4)^+$, 430 2777, calc for $C_{25}H_{40}NO_3Si$ $(M+NH_4)$, 430 2777)

2-(4-Chlorobutyloxy)tetrahydro-2*H*-pyran (18).- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (231 mg, 1 0 mmol) with 4-chloro-1-butanol (0 17 ml, 185 mg, 1 70 mmol, 1 7 equiv), $MgBr_2$ Et_2O (516 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (85 mg, 0 99 mmol, 1 0 equiv), followed by standard work-up and chromatography, gave the acetal product 18 (191 mg, 0 99 mmol, 97%) as a colourless oil, ν_{max} (film) 2940, 2868, 1441, 1351, 1276, 1260, 1200, 1136, 1120, 1076, 1034, 1022, 986, 906, 869, 814 and 651 cm^{-1}, δ_H (250 MHz) 1 48-1 95 (10H, m, 3-H_2 4-H_2 5-H_2 2'-H_2 3'-H_2), 3 42 (1H, dt, *J* 9 5 6 0 Hz, 1'-H), 3 46-3 56 (1H, m, 6-Heq), 3 58 (2H, t, *J* 6 5 Hz, 4'-H_2), 3 77 (1H, dt, *J* 9 5 6 5 Hz, 1'-H), 3 85 (1H, ddd, *J* 11 5 7 5 4 0 Hz, 6-Hax), 4 58 (1H, t, *J* 3 5 Hz, 2-H), m/z 191 $(M-H)^+$, 157 $(M-Cl)^+$, 149 $(M-C_2H_3O)^+$, 134 and 136 $(M-C_3H_5O)^+$, 115 $(M-C_3H_6Cl)^+$, 101 $(M-C_4H_8Cl)^+$, 91 and 93 $(C_4H_8Cl)^+$, 85 $(C_5H_9O)^+$ and 69 $(C_5H_9)^+$, (Observed $(M-H)^+$, 191 0840, calc for $C_9H_{16}ClO_2$ (M-H), 191 0839),

***trans*-1,2-Bis-(tetrahydro-2*H*-pyran-2-yloxy)cyclohexane (19).**- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (486 mg, 2 2 mmol, 2 2 equiv) with *trans*-1,2-cyclohexanol (113 mg, 0 97 mmol), $MgBr_2.Et_2O$ (769 mg, 3 0 mmol, 3 1 equiv) and $NaHCO_3$ (171 mg, 2 0 mmol, 2 1 equiv), followed by standard work-up and chromatography, gave the diacetal product 19 (171 mg, 0 65 mmol, 67%) as a colourless oil and an inseparable mixture of diastereoisomers, ν_{max} (film) 2936, 2869, 1448, 1362, 1200, 1117, 1066, 1033, 1020, 989, 903, 868 and 814 cm^{-1}, δ_H (250 MHz) 1 10-1 40 (4H, m) 1 43-1 95 (14H, m) 1 98-2 10 (2H, m) (3-H_2 4-H_2 5-H_2 6-H_2 2 x 3'-H_2 2 x 4'-H_2 2 x 5'-H_2), 3 39-3 78 (4H, m, 1-H 2-H 2 x 6'-H), 3 80-4 19 (2H, m, 2 x 6'-H), 4 79 (0 67H, dd, *J* 4 5 3 0 Hz) 4 86 (0 67H, br s) 4 95 (0 67H, dd, *J* 5 0 3 0 Hz) (2 x 2H), m/z 284 $(M)^+$, 226 $(M-C_3H_6O)^+$, 199 $(M-C_5H_9O)^+$, 101 $(C_5H_9O_2)^+$, 96 $(C_6H_8O)^+$, 94 $(C_6H_6O)^+$, 85 $(C_5H_9O)^+$ and 71 $(C_5H_{11})^+$ or $(C_4H_7O)^+$, (Observed M^+, 284 1988, calc for $C_{16}H_{28}O_4$ M, 284 1987)

2-[2-(3-Furyl)ethyloxy]tetrahydro-2*H*-pyran (20).- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (228 mg, 1 0 mmol, 1 0 equiv) with 2-(3-furyl)ethanol (110 mg, 0 98 mmol), $MgBr_2$ Et_2O (513 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (86 mg, 1 0 mmol, 1 0 equiv), followed by standard work-up and chromatography (Et_2O petrol, 1 12), gave the acetal product 20 (129 mg, 0 66 mmol, 67%) as a colourless oil, ν_{max} (film) 3131, 2941, 2868, 1498, 1439, 1382, 1351, 1260, 1200, 1182, 1160, 1136, 1120, 1078, 982, 965, 907, 873, 816, 781 and 729 cm^{-1}, δ_H (250 MHz) 1 46-1 90 (6H, m, 3-H_2 4-H_2 5-H_2), 2 73 (2H, t, *J* 7 0 Hz, 2'-H_2), 3 44-3 55 (1H, m, 6-Heq), 3 56 (1H, dt, *J* 9 5 7 0 Hz, 1'-H), 3 83 (1H, ddd, *J* 11 0 7 0 4 0, 6-Hax), 3 90 (1H, dt, *J* 9 5 7 0 Hz, 1'-H), 4 62 (1H, t, *J* 3 5 Hz, 2-H), 6 32 (1H, s, 4"-H), 7.28 (1H, s, 2"-H), 7 35 (1H, s, 5"-H), m/z 196 $(M)^+$, 166 $(M-CH_2O)^+$, 149 $(M-CH_3O_2)^+$, 137 $(M-C_3H_7O)^+$, 135 $(M-C_2H_5O_2)^+$, 112 $(C_6H_8O_2)^+$, 101 $(C_5H_9O_2)^+$, 95 $(C_6H_7O)^+$, 85 $(C_5H_9O)^+$, 81 $(C_5H_5O)^+$ and 67 $(C_4H_3O)^+$, (Observed M^+, 196 1099, calc for $C_{11}H_{16}O_3$ M, 196 1099)

2-(Benzyloxy)tetrahydro-2*H*-pyran (21)[1c].- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (231 mg, 1 0 mmol, 1 1 equiv) with benzyl alcohol (0 10 ml, 105 mg, 0 97 mmol), $MgBr_2$ Et_2O (511 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (89 mg, 1 1 mmol, 1 1 equiv), followed by standard work-up and chromatography (Et_2O petrol, 1 12), gave the acetal product 21 (178 mg, 0 93 mmol 95%) as a colourless oil, ν_{max} (film) 3062, 3029, 2940, 2868, 1450, 1439, 1383, 1350, 1262, 1201, 1183,

1155, 1120, 1078, 1057, 1026, 976, 906, 870, 810, 736 and 699 cm^{-1}, δ_H (250 MHz) 1 40-2 00 (6H, m, 3-H_2 4-H_2 5-H_2), 3 51-3 62 (1H, m, 6-H), 3 88-4 02 (1H, m, 6-H), 4 51 (1H, d, *J* 11 0 Hz, PhCH), 4 73 (1H, t, *J* 4 0 Hz, 2-H), 4 81 (1H, d, *J* 11 0 Hz, PhCH), 7 22-7 40 (5H, m, PhH), m/z 192 $(M)^+$, 146 $(M-C_2H_6O)^+$, 101 $(C_5H_9O_2)^+$, 91 $(C_7H_7)^+$ and 85 $(C_5H_9O)^+$, (Observed M^+, 192 1150, calc for $C_{12}H_{16}O_2$ M, 192 1150)

5-(Tetrahydro-2*H*-pyran-2-yloxy)pentan-2-one (22).- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (226 mg, 1 0 mmol) with 5-hydroxy-pentane-1-one (201 mg, 2 0 mmol, 2.0 equiv), $MgBr_2$ Et_2O (508 mg, 2.0 mmol, 2 0 equiv) and $NaHCO_3$ (89 mg, 1 1 mmol, 1 1 equiv), followed by standard work-up and chromatography (gradient elution, Et_2O petrol, 1 10-1 5), gave the acetal product **22** (156 mg, 0 84 mmol, 84%) as a colourless oil, ν_{max} (film) 3512, 2942, 2869, 1709, 1439, 1354, 1200, 1164, 1136, 1120, 1076, 1034, 974, 906, 870 and 814 cm^{-1}; δ_H (250 MHz) 1 45-1 91 (8H, m, 4-H_2 3'-H_2 4'-H_2 5'-H_2), 2 13 (3H, s, 1-H_3), 2 52 (2H, t, *J* 7 5 Hz, 3-H_2), 3 38 (1H, dt, *J* 9 5 6 0 Hz, 5-H), 3 42-3 52 (1H, m, 6'-H), 3 71 (1H, dt, *J* 9 5 6 5 5-H), 3 77-3 86 (1H, m, 6'-H), 4 53 (1H, t, *J* 3 5 Hz, 2'-H), m/z 101 $(C_5H_9O_2)^+$, and 85 $(C_5H_9O)^+$, (Observed $(M+NH_4)^+$, 204 1596, calc for $C_{10}H_{22}NO_3$ $(M+NH_4)$, 204 1600), (Found C, 64 78, H, 9 97, calc for $C_{10}H_{18}O_3$, C, 64 49, H, 9 74%)

2-(Diphenylmethyloxy)tetrahydro-2*H*-pyran (23)[1d].- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (227 mg, 1 0 mmol) with 1,1-diphenylmethanol (186 mg, 1 0 mmol, 1 0 equiv), $MgBr_2.Et_2O$ (521 mg, 2 0 mmol, 2.0 equiv) and $NaHCO_3$ (91 mg, 1 1 mmol, 1 0 equiv), followed by standard work-up and chromatography, gave the acetal product **23** (179 mg, 0 67 mmol, 67%) as a colourless solid, m p 55-57°C, ν_{max} (film) 3058, 3026, 2939, 2869, 1490, 1448, 1200, 1183, 1118, 1077, 1020, 976, 908, 762, 742 and 700 cm^{-1}, δ_H (250 MHz) 1 40-2 00 (6H, m, 3-H_2 4-H_2 5-H_2), 3 42-3 54 (1H, m, 6-H), 3.82-3 92 (1H, m, 6-H), 4 66 (1H, t, *J* 6 5 Hz, 2-H), 5 80 (1H, s, Ph_2CH), 7 14-7 40 (10H, m, PhH), m/z 268 $(M)^+$, 222 $(M-C_2H_6O)^+$, 184 $(Ph_2CHOH)^+$, 167 $(Ph_2CH)^+$, 105 $(PhCO)^+$, 85 $(C_5H_9O)^+$ and 77 $(Ph)^+$, (Observed M^+, 268 1463, calc for $C_{18}H_{20}O_2$ M, 268 1463), (Found C, 80 67, H, 7 69, calc for $C_{18}H_{20}O_2$, C, 80 56, H, 7 51%)

Tetrahydro-2-(phenoxy)-2*H*-pyran (24)[1f].- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (230 mg, 1 0 mmol, 1 0 equiv) with phenol (94 mg, 1 0 mmol), $MgBr_2$ Et_2O (527 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (87 mg, 1 0 mmol, 1 0 equiv), followed by standard work-up and chromatography, gave the acetal product **24** (84 mg, 0 47 mmol, 47%) as a colourless oil, ν_{max} (film) 3063, 3037, 2942, 2872, 2850, 1587, 1491, 1450, 1439, 1387, 1355, 1288, 1232, 1202, 1182, 1172, 1123, 1111, 1077, 1038, 1021, 1000, 964, 921, 872, 810 and 690 cm^{-1}, δ_H (250 MHz) 1 58-1 73 (3H, m) 1 83-1 90 (2H, m) (3-Hax 4-H_2 5-H_2), 1 96-2 06 (1H, m, 3-Heq),3 61 (1H, ddd, *J* 11 5 5 5 4.0 Hz, 6-Heq), 3 93 (1H, m, *J* 11.5 9 0 3 0 Hz, 6-Hax), 5 43 (1H, t, *J* 3 0 Hz, 2-H), 6 95-7 09 (3H, m) and 7 24-7 32 (2H, m) (PhH), m/z 178 $(M)^+$, 184 $(PhOH)^+$ and 85 $(C_5H_9O)^+$, (Observed M^+, 178 0994, calc for $C_{11}H_{14}O_2$ M, 178 0994)

Tetrahydro-2-methoxy-6-phenyl-2*H*-pyran (25).- Reaction of *trans*-tetrahydro-2-phenyl-6-(phenylsulphonyl)-2*H*-pyran (3) (302 mg, 1 0 mmol) with methanol (81 µl, 64 mg, 2 0 mmol, 2 0 equiv), $MgBr_2$ Et_2O (517 mg, 2 0 mmol, 2 0 equiv) and $NaHCO_3$ (84 mg, 1 00 mmol, 1 0 equiv) at room temperature overnight gave no reaction as detected by t.l.c However, sonication of the reaction mixture for six hours, followed by standard work-up and chromatography gave the acetal product (**25**) (135 mg, 0 70 mmol, 70%) (*cis trans* 20 80) as a colourless oil, ν_{max} (film) 2941, 1125, 1061, 1028, 951, 754, and 699 cm^{-1}, δ_H (250 MHz) 1 40-2 10 (6H, m, 3-H_2 4-H_2 5-H_2), 3 42 (2 4H, s, *trans* isomer OCH_3), 3 53 (0 6H, s, *cis* isomer OMe), 4 46 (0 2H, dd, *J* 10 0 2 0 Hz, *cis* isomer 6-H), 4 49 (0 2H, dd, *J* 9 5 2 0 Hz, *cis* isomer 2-H), 4 76 (0 8H, dd, *J* 11 0 2 5 Hz, *trans* isomer 6-H), 4 88 (0 8H, dd, *J* 2 5 2 0 Hz, *trans* isomer 2-H), and 7 25-7 40 (5H, m, PhH), m/z 192 $(M)^+$, 162 $(M-CH_2O)^+$, 161 $(M-CH_3O)^+$, 105 $(M-C_5H_9O)^+$, 104 $(M-C_5H_{10}O)^+$ and 58 $(C_3H_6O)^+$, (Found C, 74 96, H, 8 41 $C_{12}H_{16}O_2$ requires C, 74 97, H, 8 39%)

***trans*- and *cis*-2-(*tert*-Butyloxy)tetrahydro-6-phenyl-2*H*-pyran (26) and (27).**- Reaction of *trans*-tetrahydro-6-phenyl-2-(phenylsulphonyl)-2*H*-pyran (3) (151 mg, 0 50 mmol) with *tert*-butanol (52 µl, 41 mg, 0 55 mmol, 1 1 equiv), $MgBr_2$ Et_2O (262 mg, 1 01 mmol, 2 0 equiv) and $NaHCO_3$ (44 mg, 0 52 mmol, 1 0 equiv), followed by standard work-up and chromatography (Et_2O petrol, 1 50) gave the 2,6-*trans*-acetal product **26** (47 mg, 0 20 mmol, 40%) as a white solid, m p 50-55°C, ν_{max} (film) 2971, 2939, 1367, 1195, 1163, 1118, 1110, 1029, 993, 753 and 678 cm^{-1}, δ_H (250 MHz) 1 26 (9H, s, $C(CH_3)_3$), 1 51-1 88 (5H, m, 3-Hax 4-H_2 5-H_2), 1 97-2 14 (1H, m, 3-Heq), 4 97 (1H, dd, *J* 11 5 2 5 Hz, 6-Hax), 5 29 (1H, d, *J* 3 0 Hz, 2-

Heq) 7.21-7 39 (5H, m, PhH), m/z 234 $(M)^+$, 219 $(M\text{-}CH_3)^+$, 206 $(M\text{-}C_2H_4)^+$, 178 $(M+H\text{-}^tBu)^+$, 161 $(M\text{-}^tBuO)^+$, 107 $(C_7H_7O)^+$, 104 $(C_8H_8)^+$, 91 $(C_7H_7)^+$, 77 (C_6H_5), and 57 (^tBu), (Observed $(M+NH_4)^+$, 252 1963, calc for $C_{15}H_{26}NO_2$ $(M+NH_4)$, 252 1964); (Found. C, 76.87, H, 9 60, $C_{15}H_{22}O_2$ requires C, 76 88, H, 9 46%) Further elution gave the 2,6-*cis*-acetal product **27** (44 mg, 0 19 mmol, 38%) as a white waxy solid, ν_{max} (film) 2935, 2854, 1450, 1138, 1073, 1024, 963, 755 and 698 cm^{-1}, δ_H (250 MHz) 1 29 (9H, s, CMe_3), 1 40-1 98 (6H, m, 3-H_2 4-H_2 5-H_2), 4 46 (1H, dd, *J* 11 0 2 0 Hz, 6-Hax), 4.78 (1H, dd, *J* 9 0 2 0 Hz, 2-Hax) 7 21-7 41 (5H, m, PhH), m/z 234 $(M)^+$, 206 $(M\text{-}C_2H_4)^+$, 188 $(M\text{-}C_2H_6O)^+$, 177 $(M\text{-}^tBu)^+$, 161 $(M\text{-}^tBuO)^+$, 107 $(C_7H_7O)^+$, 104 $(C_8H_8)^+$, 91 $(C_7H_7)^+$, 77 $(C_6H_5)^+$ and 57 (^tBu), (Observed M^+, 234 1620, calc for $C_{15}H_{22}O_2$ M, 234 1620)

***trans*- and *cis*-2-Cyclohexyloxy-6-phenyltetrahydro-2*H*-pyran (28) and (29).**- Reaction of *trans*-tetrahydro-6-phenyl-2-(phenylsulphonyl)-2*H*-pyran (3) (155 mg, 0 51 mmol) with cyclohexanol (58 µl, 56 mg, 0 56 mmol, 1 1 equiv), $MgBr_2$ Et_2O (259 mg, 1 00 mmol, 2 0 equiv) and $NaHCO_3$ (60 mg, 0 71 mmol, 1 4 equiv) under ultrasound conditions overnight, followed by standard work-up and chromatography (petrol) gave the 2,6-*trans*-acetal product **28** (82 mg, 0 31 mmol, 62%) as a colourless solid, m p 38-40°C, ν_{max} (film) 3059, 3027, 2930, 2854, 1602, 1491, 1448, 1357, 1260, 1210, 1171, 1121, 1062, 1032, 998, 950, 894, 754 and 698 cm^{-1}, δ_H (250 MHz) 1 42 (1H, ddd, *J* 22 5 11 5 3 5 Hz, 4-Hax), 1 52 (1H, dd, *J* 9 0 4 5 Hz, 3-Hax), 1 17-1.32 (5H, m) and 1 59-1 81 (6H, m) (4-Heq 2'-H_2 3'-H_2 4'-H_2 5'-H_2 6'-H_2), 1 84-1 92 (2H, m) and 2 00-2 09 (1H, m) (3-H 5-H_2), 3 63 (1H, tt, *J* 9 5 4 0 Hz, 1'-H), 4 86 (1H, dd, *J* 11 5 2 0 Hz, 6-Hax), 5 14 (1H, d, *J* 3 0 Hz, 2-Heq) 7 24-7 37 (5H, m, PhH), m/z 260 $(M)^+$, 232 $(M\text{-}C_2H_4)^+$, 177 $(M\text{-}C_6H_{11})^+$, 161 $(M\text{-}C_6H_{11}O)^+$, 154 $(M\text{-}C_7H_6O)$, 132 (C_9H_8O), 126 $(C_8H_{14}O)^+$, 117 $(C_9H_9)^+$, 107 $(C_7H_6O)^+$, 104 $(C_8H_8)^+$, 91 $(C_7H_7)^+$, 82 $(C_6H_{10})^+$ and (C_5H_6O), and 55 (C_4H_7), (Observed M^+, 260 1776, calc for $C_{17}H_{24}O_2$ M, 260 1776), (Found C, 78 47, H, 9 58, $C_{17}H_{24}O_2$ requires C, 78 42, H, 9 29%) Further elution gave the 2,6-*cis*-acetal product **29** (15 mg, 0 058 mmol, 11%) as a colourless solid, m p 82-84°C, ν_{max} (film) 2929, 2853, 1448, 1361, 1138, 1064 and 1012 cm^{-1}, δ_H (250 MHz) 1 17-1 58 (8H, m, 4-H_2 3'-H_2 4'-H_2 5'-H_2), 1 65-1 83 (5H, m, 3-Heq 2'-H_2 6'-H_2), 1 91-2 01 (3H, m, 3-Hax, 5-H_2), 3 72 (1H, tt, *J* 9 5 4 0 Hz, 1'-H), 4 46 (1H, dd, *J* 11 5 2 0 Hz, 6-Hax), 4 71 (1H, dd, *J* 9 6 2 0 0 Hz, 2-Hax) 7 24-7 41 (5H, m, PhH), m/z 260 $(M)^+$, 232 $(M\text{-}C_2H_4)^+$, 177 $(M\text{-}C_6H_{11})^+$, 161 $(M\text{-}C_6H_{11}O)^+$, 154 $(M\text{-}C_7H_6O)$, 132 (C_9H_8O), 126 $(C_8H_{14}O)^+$, 117 (C_9H_9), 107 $(C_6H_6O)^+$, 104 $(C_8H_8)^+$, 91 $(C_7H_7)^+$, 82 $(C_6H_{10})^+$ and (C_5H_6O), and 55 (C_4H_7), (Observed M^+, 260 1776, calc for $C_{17}H_{24}O_2$ M, 260 1776), (Found C, 78 67, H, 9 58, $C_{17}H_{24}O_2$ requires C, 78 42, H, 9 29%)

***trans*- and *cis*-6-(Cyclohexyloxy)tetrahydro-2*H*-pyran-2-methanol acetate (30) and (31).**- Reaction of *trans*-6-(phenylsulphonyl)-tetrahydro-2*H*-pyran-2-methanol acetate (**4**) (151 mg, 0 51 mmol) with cyclohexanol (58 µl, 56 mg, 0 56 mmol, 1 1 equiv), $MgBr_2$ Et_2O (257 mg, 1 00 mmol, 2 0 equiv) and $NaHCO_3$ (43 mg, 0 51 mmol, 1 0 equiv) for four days at room temperature, followed by standard work-up and chromatography (gradient elution, Et_2O petrol, 1 20-1 10) gave the 2,6-*cis*-acetal product **30** (76 mg, 0 30 mmol, 58%) as a colourless oil, ν_{max} (film) 2933, 2854, 1743, 1448, 1366, 1234, 1205, 1120, 1062, 1039, 1024, 1004, 953, and 867 cm^{-1}, δ_H (250 MHz) 1 16-1 41 (6H, m) and 1 53-1 68 (5H, m) (3-H_2 4-H_2 5-Hax 3'-H_2 4'-H_2 5'-H_2), 1 72-1 77 (2H, m, 2'-Hax 6'-Hax), 1 88-1 92 (3H, m, 5-Heq 2'-Heq 6'-Heq), 2 07 (3H, s, CH_3CO), 3 57 (1H, tt, *J* 9 5 4 0 Hz, 1'-H), 3 98-4 09 (3H, m, 1-H_2 2-H), 5 02 (1H, s, 6-Heq), m/z 256 $(M)^+$, 213 $(M\text{-}CH_3CO)^+$, 196 $(M\text{-}CH_3CO_2H)^+$, 183 $(M\text{-}CH_3CO_2CH_2)^+$, 173 $(M\text{-}C_6H_{11})^+$, 157 $(M\text{-}C_6H_{11}O)^+$, 128 $(C_7H_{12}O_2)^+$, 114 $(C_6H_{10}O_2)^+$, 101 $(C_6H_{13}O)^+$ and $(C_5H_9O_2)^+$, 83 $(C_6H_{11})^+$ and 43 (C_2H_3O), (Observed M^+, 256 1675, calc for $C_{14}H_{24}O_4$ M, 256 1674), (Found C, 65 48, H, 9 69, $C_{14}H_{24}O_4$ requires C, 65 60, H, 9 44%) Further elution gave the 2,6-*trans*-acetal product **31** (23 mg, 0 090 mmol, 18%) as a colourless oil, ν_{max} (film) 2931, 2855, 1741, 1448, 1364, 1233, 1200, 1164, 1074, 1032, 964, 900 and 845 cm^{-1}, δ_H (250 MHz) 1 15-1 55 (10H, m, 3-H_2 4-H_2 3'-H_2 4'-H_2 5'-H_2), 1 71-1 76 (3H, m, 5-Hax 2'-Hax 6'-Hax), 1 81-1 90 (2H, m, 2'-Heq 6'-Heq), 1 97 (1H, br d, *J* 9 5 Hz, 5-Heq), 2 06 (3H, s, CH_3CO), 3 60-3 66 (2H, m, 2-H 1'-H), 4 06 (1H, dd, *J* 11 5 4 5 Hz, 1-H), 4 15 (1H, dd, *J* 11 5 6 5 Hz, 1-H), 4 52 (1H, dd, *J* 9 5 2 0 Hz, 6-Hax), m/z 255 $(M\text{-}H)^+$, 237 $(M\text{-}H_2O)^+$, 213 $(M\text{-}CH_3CO)^+$, 196 $(M\text{-}CH_3CO_2H)^+$, 183 $(M\text{-}CH_3CO_2CH_2)^+$, 173 $(M\text{-}C_6H_{11})^+$, 157 $(M\text{-}C_6H_{11}O)^+$, 101 $(C_6H_{13}O)^+$ and $(C_5H_9O_2)^+$ and 43 (C_2H_3O), (Observed $(M\text{-}H)^+$, 255 1596, calc for $C_{14}H_{23}O_4$ (M-H), 255 1596), (Found. C, 65 42, H, 9 61, $C_{14}H_{24}O_4$ requires C, 65 60, H, 9 44%)

[2α,6β(*E*)]- and [2α,6α(*E*)]-6-(3,7-Dimethyl-2,6-octadienyloxy)tetrahydro-2*H*-pyran-2-methanol acetate (32) and (33).- Reaction of *trans*-6-(phenylsulphonyl)-tetrahydro-2*H*-pyran-2-methanol acetate (4) (149 mg, 0.50 mmol) with geraniol (95 µl, 84 mg, 0 54 mmol, 1 1 equiv), $MgBr_2$ Et_2O (256 mg, 0 99 mmol, 2 0 equiv) and $NaHCO_3$ (48 mg, 0 57 mmol, 1 1 equiv) for four days at room temperature, followed by standard work-up and chromatography (gradient elution, Et_2O-petrol, 1 20-1 10) gave the 2,6-*trans*-acetal product **32** (91 mg, 0 29 mmol, 59%) as a colourless oil; ν_{max} (film) 2938, 1743, 1668, 1439, 1367, 1234, 1205, 1119, 1050, 1017, 963 and 866 cm^{-1}, δ_H (500 MHz) 1 38 (1H, ddd, *J* 24 5 13.0 4 0 Hz, 4-Hax), 1 60 (3H, s, 3'-Me), 1 68 and 1 68 (2 x 3H, 2 x s, 7'-Me_2), 1 55-1 92 (5H, m, 3-H_2 4-Heq 5-H_2), 2 02-2 20 (4H, m, 4'-H_2 5'-H_2), 2 08 (3H, s, CH_3CO), 3 97-4 05 (1H, m, 2-H), 4 00 (1H, dd, *J* 11 5 7.5 Hz, 1'-H), 4 06 (2H, d, *J* 5 0 Hz, 1-H_2), 4 19 (1H, ddd, *J* 12 0 6 5 0 5 Hz, 1'-H), 4 90 (1H, s, 6-Heq), 5 09 (1H, tt, *J* 7 0 1 5 Hz, 6'-H), 5 36 (1H, tt, *J* 6 5 1 0 Hz, 2'-H), m/z 310 $(M)^+$, 292 $(M-H_2O)^+$, 173 $(M-C_{10}H_{17})^+$, 157 $(M-C_{10}H_{17}O)^+$, 136 $(C_{10}H_{16})^+$, 97 $(C_7H_{13})^+$, 69 $(C_5H_9)^+$ and 43 (C_2H_3O), (Observed M^+, 310 2144, calc for $C_{18}H_{30}O_4$ M, 310 2144) Further elution gave the 2,6-*cis*-acetal product **33** (40 mg, 0 13 mmol, 26%) as a colourless oil, ν_{max} (film) 2941, 2857, 1742, 1664, 1441, 1367, 1234, 1199, 1153, 1139, 1074, 1037, 998, 954, 898 and 827 cm^{-1}; δ_H (500 MHz) 1 27 (1H, ddd, *J* 25 0 13 5 4 0 Hz, 4-Hax), 1 38-1 46 (1H, m) and 1 49-1 57 (2H, m) (3-Hax 4-Heq 5-Hax), 1 60 (3H, s, 3'-Me), 1 68 (6H, s, 7'-Me_2), 1 74-1 77 (1H, m) and 1 85-1 93 (1H, m) (3-Heq 5-Heq), 1 95-2 11 (4H, m, 4'-H_2 5'-H_2), 2 07 (3H, s, CH_3CO), 3 60-3 66 (1H, m, 2-H), 4 09 (1H, dd, *J* 11 5 4 5 Hz, 1-H), 4 14 (1H, dd, *J* 11 5 6 5 Hz, 1-H), 4 20 (1H, dd, *J* 12 0 8 0 Hz, 1'-H), 4.29 (1H, dd, *J* 12 0 6 0 Hz, 1'-H), 4 43 (1H, dd, *J* 9 5 2 0 Hz, 6-Hax), 5 08 (1H, tq, *J* 7 0 1 5 Hz, 6'-H), 5 34 (1H, tt, *J* 6 5 1 0 Hz, 2'-H), m/z 310 $(M)^+$, 292 $(M-H_2O)^+$, 173 $(M-C_{10}H_{17})^+$, 157 $(M-C_{10}H_{17}O)^+$, 136 $(C_{10}H_{16})^+$, (Observed M^+, 310 2144, calc for $C_{18}H_{30}O_4$ M, 310 2144), (Found C, 69 89, H, 9 96, $C_{18}H_{30}O_4$ requires C, 69 64, H, 9 74%)

***trans*- and *cis*-Tetrahydro-6-phenoxy-2*H*-pyran-2-methanol acetate (34) and (35).-** Reaction of *trans*-6-(phenylsulphonyl)-tetrahydro-2*H*-pyran-2-methanol acetate (4) (283 mg, 0.95 mmol) with phenol (94 mg, 1 00 mmol, 1 1 equiv), $MgBr_2$ Et_2O (514 mg, 1 99 mmol, 2 1 equiv) and $NaHCO_3$ (87 mg, 1 04 mmol, 1 1 equiv), followed by non-basic work-up and chromatography on alumina (Et_2O petrol, 1 9) gave the 2,6-*trans*-acetal product **34** (92 mg, 0 37 mmol, 39%) as a colourless oil, ν_{max} (film) 2945, 2873, 1740, 1597, 1587, 1492, 1453, 1439, 1366, 1232, 1206, 1173, 1114, 1045, 1000, 963, 870, 757 and 693 cm^{-1}, δ_H (250 MHz) 1 48-2 11 (6H, m, 3-H_2 4-H_2 5-H_2), 1 96 (3H, s, CH_3CO), 3 98-4 08 (1H, m, 2-H), 4 04 (2H, dd, *J* 3 0 2 0 Hz, 1-H_2), 5 61 (1H, br s, 6-Heq), 6 98 (1H, tt, *J* 7 5 1 0 Hz, *p*-PhH), 7 09 (2H, dd, *J* 9 0 1 0 Hz, 2 x *o*-PhH), 7 23-7 31 (2H, m *m*-PhH), m/z 250 $(M)^+$, 177 $(M-CH_3CO_2CH_2)^+$, 157 $(M-PhO)^+$, 97 $(C_6H_9O)^+$ and 43 (C_2H_3O), (Observed M^+, 250 1205, calc for $C_{14}H_{18}O_4$ M, 250 1205), (Found C, 67 34, H, 7 40, $C_{14}H_{18}O_4$ requires C, 67 18, H, 7 25%) Further elution gave the 2,6-*cis*-acetal product **35** (26 mg, 0 10 mmol, 11%) as a colourless oil, ν_{max} (film) 2922, 2851, 1739, 1587, 1490, 1459, 1367, 1236, 1195, 1070, 1037, 753 and 690 cm^{-1}, δ_H (250 MHz) 1 25-1 46 (1H, m, 4-Hax), 1 55-1 81 (3H, m, 3-H_2 4-Heq), 1 94-2 05 (2H, m, 5-H_2), 2 05 (3H, s, CH_3CO), 3 85 (1H, dddd, *J* 11 0 6 5 4 5 2 5 Hz, 2-H), 4 13 (1H, d, *J* 2 0 Hz, 1-H), 4 16 (1H, d, *J* 4 5 Hz, 1-H), 5 09 (1H, dd, *J* 8 5 2 0 Hz, 6-Hax), 6 96-7 05 (3H, m) 7 22-7 30 (2H, m) (PhH), m/z 250 $(M)^+$, 177 $(M-CH_3CO_2CH_2)^+$, 157 $(M-PhO)^+$, 97 $(C_6H_9O)^+$ and 43 (C_2H_3O), (Observed M^+, 250 1205, calc for $C_{14}H_{18}O_4$ M, 250 1205)

(2*R*,3*S*,6*RS*)-3-Acetoxy-6-benzyloxy-3,6-dihydro-2*H*-pyran-2-methanol acetate (36).- Reaction of (2*R*,3*S*,6*R*)-3-acetoxy-3,6-dihydro-6-(phenylsulphonyl)-2*H*-pyran-2-methanol acetate (5) (27 mg, 0 076 mmol) with benzyl alcohol (40 µl, 42 mg, 0 39 mmol, 5 1 equiv), $MgBr_2$ Et_2O (39 mg, 0 15 mmol, 2 0 equiv) and $NaHCO_3$ (14 mg, 0 17 mmol, 2 2 equiv) in dry distilled THF (2 0 ml) at room temperature overnight gave no reaction as detected by t l c However, sonication of the reaction mixture for three days, followed by standard work-up and chromatography (Et_2O petrol, 1 9), gave the glycoside product **36** (17 mg, 0 053 mmol, 70%) as a colourless oil and an inseparable mixture of diastereoisomers (1*S* 1*R*, 22 78), ν_{max} (film) 2926, 2855, 1742, 1451, 1369, 1235, 1039, 733 and 699 cm^{-1}, δ_H (500 MHz) 2 08 (3H, s, *minor/major* CH_3CO), 2 08 (0 66H, s, *minor* CH_3CO), 2 10 (2 34H, s, *major* CH_3CO), 4 06-4 33 (3H, m, *minor/major* 1-H_2 2-H), 4 60 (0 78H, d, *J* 11 5 Hz, *major* PhCH), 4 62 (0 22H, d, *J* 12 0 Hz, *minor* PhCH), 4 81 (0 78H, d, *J* 11 5 Hz, *major* PhCH), 4 88 (0 22H, d, *J* 12.0 Hz, *minor* PhCH), 5 14 (0 78H, t, *J* 1 0 Hz, *major* 6-Heq), 5 19-5 21 (0 44H, m, *minor* 3-H *minor* 6-Hax), 5 34 (0 78H, dq, *J* 9 5 1 5 Hz, *major* 3-H), 5 85 (0 78H, ddd, *J* 10 5 2 5 2 0 Hz, *major* 4-H), 5 90 (0 78H, dd, *J* 10 0 0 5 Hz, *major* 5-H), 5 97 (0 22H, dd, *J* 10 5 1 0 Hz, *minor* 4-H), 6 01 (0 22H, ddd, *J* 10 0 3 5 1 5 Hz, *minor* 5-H), 7 28-7 71 (5H, m, PhH), m/z 302 $(M-H_2O)^+$, 279 $(M+H_2-CH_3CO)^+$, 261 $(M-CH_3CO_2)^+$, 242 $(M-PhH)^+$, 229 $(M-PhCH_2)^+$, 218 $(M-CH_3CO_2-CH_3CO)^+$, 213 $(M-PhCH_2O)^+$,

200 ($C_{13}H_{12}O_2$)$^+$, 187 ($C_8H_{11}O_5$)$^+$, 176 ($C_{11}H_{12}O_2$)$^+$, 153 ($C_8H_9O_3$)$^+$, 111 ($C_6H_7O_2$)$^+$, 94 (C_6H_6O)$^+$, 91 (C_7H_7)$^+$ and 43 (C_2H_3O); (Observed (M+NH_4)$^+$, 338 1604, calc for $C_{17}H_{24}NO_6$ (M+NH_4), 338.1603)

(2*R*,3*S*,6*RS*)-3-Acetoxy-6-cyclohexyloxy-3,6-dihydro-2*H*-pyran-2-methanol acetate (37).- Reaction of (2*R*,3*S*,6*R*)-3-acetoxy-3,6-dihydro-6-(phenylsulphonyl)-2*H*-pyran-2-methanol acetate (5) (88 mg, 0 25 mmol) with cyclohexanol (50 µl, 48 mg, 0 48 mmol, 1 9 equiv), $MgBr_2.Et_2O$ (128 mg, 0 50 mmol, 2 0 equiv) and $NaHCO_3$ (22 mg, 0.26 mmol, 1 1 equiv.) in dry distilled THF (1 0 ml) under ultrasound conditions overnight, followed by standard work-up and chromatography (Et_2O petrol, 1 4), gave the glycoside product 37 (59 mg, 0 19 mmol, 76%) as a colourless oil and an inseparable mixture of diastereoisomers (6*R* 6*S*, 13 87), ν_{max} (film) 2931, 2855, 1742, 1448, 1389, 1232, 1185, 1102, 1035, 982 and 742 cm^{-1}, δ_H (500 MHz, 6*S* isomer only seen clearly) 1 15-1 45 (6H, m, 3'-H_2 4'-H_2 5'-H_2), 1 73-1 77 (2H, m, 2'-Hax 6'-Hax), 1 88-2 00 (2H, m, 2'-Heq 6'-Heq), 2 07 (3H, s, CH_3CO), 2 09 (3H, s, CH_3CO), 3 64 (1H, ddd, *J* 13 5 9 5 4 0 Hz, 1'-H), 4 13-4 20 (2H, m, 1-H 2-H), 4 23 (1H, dd, *J* 12 0 6 0 Hz, 1-H), 5.17 (1H, d, *J* 2 5 Hz, 6-Heq), 5 29 (1H, ddd, *J* 9 5 3 0 1 5 Hz, 3-H), 5 81 (1H, ddd, *J* 10 0 2 5 2 0 Hz, 4-H), 5 86 (1H, br d, *J* 10 5 Hz, 5-H), m/z 312 (M)$^+$, 270 (M+H-CH_3O)$^+$, 252 (M-CH_3CO_2H)$^+$, 239 (M-$CH_3CO_2CH_2$)$^+$, 213 (M-$C_6H_{11}O$)$^+$, 211 (M+H-CH_3CO_2-CH_3CO)$^+$, 168 ($C_8H_8O_4$)$^+$, 153 ($C_8H_9O_3$)$^+$, and 128 ($C_6H_{11}OCHO$)$^+$, (Observed (M+NH_4)$^+$, 330 1917, calc for $C_{16}H_{28}NO_6$ (M+NH_4), 330 1916), (Found C, 61 47, H, 7 88, $C_{16}H_{24}O_6$ requires C, 61 52, H, 7 74%)

(*E*)-(3,7-Dimethyl-2,6-octadienyl)-4-*O*-(*tert*-butyldimethylsilyl)-L-oleandroside (38).- Reaction of 4-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1-(phenylsulphonyl)-α-L-oleandrose (6) (41 mg, 0 10 mmol) with geraniol (85 µl, 76 mg, 0 49 mmol, 4 9 equiv), $MgBr_2$ Et_2O (127 mg, 0 49 mmol, 4 9 equiv) and $NaHCO_3$ (47 mg, 0 56 mmol, 5 6 equiv) in dry distilled THF (2 0 ml) at room temperature overnight gave no reaction as detected by t.l c However, heating of the reaction mixture at 50°C overnight, followed by standard work-up and chromatography (gradient elution, Et_2O-petrol, 1 15-1 6), gave the glycoside product 38 (24 mg, 0 058 mmol, 58%) as a colourless oil and an inseparable mixture of diastereoisomers (1*S* 1*R*, 33 67), ν_{max} (film) 2929, 2355, 1666, 1456, 1384, 1358, 1248, 1201, 1145, 1104, 1075, 1016, 989, 893, 873, 836, 777 and 666 cm^{-1}, δ_H (500 MHz) 0 07 (1H, s, *minor* SiMe), 0 08 (2H, s, *major* SiMe), 0 08 (1H, s, *minor* SiMe), 0 09 (2H, s, *major* SiMe), 0 89 (3H, s, *minor* Si^{t}Bu), 0 90 (6H, s, *major* Si^{t}Bu), 1 25 (2H, d, *J* 6 5 Hz, *major* 5-Me), 1 30 (1H, d, *J* 6 5 Hz, *minor* 5-Me), 1 57 (2H, s, *major* 3'-Me), 1 61 (1H, s, *minor* 3'-Me), 1 68 (4H, s, *major* 7'-Me_2), 1 69 (2H, s, *minor* 7'-Me_2), 1 41-1 72 (1H, m, *minor/major* 2-Hax), 2 04 and 2 10 (2 x 2H, 2 x t, *J* 7 5 Hz, *minor/major* 4'-H_2 5'-H_2), 2 27 (0 67H, dd, *J* 13 0 5 0 Hz, *major* 2-Heq), 2 32 (0 33H, ddd,*J* 12 5 4 5 2 0 Hz, *minor* 2-Heq), 3 13 (1H, t, *J* 8 5 Hz, *minor/major* 4-H), 3 05-3 25 (0 67H, m, *minor* 3-H 5-H), 3 30 (3H, s, *minor/major* 3-OMe), 3 40 (0 67H, ddd, *J* 11 5 8 5 5 0 Hz, *major* 3-H), 3 65 (0 67H, dq, *J* 9 0 6 5 Hz, *major* 5-H), 3 97 (0 67H, dd, *J* 12 0 7 5 Hz, *major* 1'-H), 4 10 (0 67H, dd, *J* 12 0 6 0 Hz, *major* 1'-H), 4 16 (0 33H, dd, *J* 12 0 8 0 Hz, *minor* 1'-H), 4 28 (0 33H, dd, *J* 12 0 6 0 Hz, *minor* 1'-H), 4 46 (0 33H, dd, *J* 10 0 2 0 Hz, *minor* 1-Hax), 4 88 (0 67H, d, *J* 3 5 Hz, *major* 1-Heq), 5 07-5 10 (1H, m, *minor/major* 6'-H), 5 31-5 34 (1H, m, *minor/major* 2' H), m/z 412 (M)$^+$, 394 (M-H_2O)$^+$, 380 (M-CH_3OH)$^+$, 355 (M-^{t}Bu)$^+$, 259 (M-$C_{10}H_{17}O$)$^+$, 227 (M-CH_3OH-$C_{10}H_{17}O$)$^+$, 187 (M-CH_3OH-^{t}Bu-$C_{10}H_{17}O$)$^+$, 137 ($C_{10}H_{17}$)$^+$, and 126 ($C_7H_{10}O_2$)$^+$, (Observed (M+NH_4)$^+$, 430 3353, calc for $C_{23}H_{48}NO_4Si$ (M+NH_4), 430 3352)

Methyl 4-*O*-[4-*O*-(*tert*-butyldimethylsilyl)-L-oleandrosyl]-L-oleandroside (39).- Reaction of 4-*O*-(*tert*-butyldimethylsilyl)-1-deoxy-1-(phenylsulphonyl)-α-L-oleandrose (6) (41 mg, 0 10 mmol) with methyl L-oleandroside (40 mg, 0 23 mmol, 2 2 equiv), $MgBr_2$ Et_2O (56 mg, 0 22 mmol, 2 1 equiv) and $NaHCO_3$ (18 mg, 0 21 mmol, 2.1 equiv) in dry distilled THF (2 0 ml) under ultrasound conditions overnight, followed by standard work-up and chromatography (Et_2O petrol, 1 9), gave the glycoside product 39 (29 mg, 0 067 mmol, 65%) as a colourless oil and an inseparable mixture of diastereoisomers at the two anomeric positions, ν_{max} (film) 2930, 2898, 2856, 1456, 1384, 1361, 1300, 1251, 1206, 1103, 1054, 985, 931, 895, 837, 778, 745 and 667 cm^{-1}, δ_H (500 MHz, major α,α isomer only) 0 07 (3H, s, SiMe), 0 09 (3H, s, SiMe), 0 89 (9H, s, Si^{t}Bu), 1 21 (3H, d, *J* 6 5 Hz) and 1 29 (3H, d, *J* 6 0 Hz) (5-Me 5'-Me), 1 48 (1H, ddd, *J* 13 0 11 5 4 0 Hz) and 1 52 (1H, ddd, *J* 13 0 11 5 4 0 Hz) (2-Hax 2'-Hax), 2 24 (1H, ddd, *J* 13 0 5 0 1 0 Hz) and 2 28 (1H, ddd, *J* 13 0 5 0 1 0 Hz) (2-Heq 2'-Heq), 3 13 (1H, t, *J* 9 0 Hz) and 3 20 (1H, t, *J* 9 0 Hz) (4-H 4'-H), 3 31 (6H, s) and 3 35 (3H, s) (β-OMe 1'-OMe 3'-OMe), 3 27-3 41 (1H, m) and 3 56 (1H, ddd, *J* 11 5 8 5 5 0 Hz) (3-H 3'-H), 3 64 (1H, dq, *J* 9 5 6 0 Hz) and 3 69 (1H, dq, *J* 9 0 6 5 Hz) (5-H 5'-H), 4 74 (1H, d, *J* 2 5 Hz, 1'-Heq), 5 30 (1H, d, *J* 3 0 Hz, 1-Heq), m/z 433 (M-H)$^+$, 403 (M-CH_3O)$^+$, 377 (M-^{t}Bu)$^+$, 333 (M-$C_5H_9O_2$)$^+$, 301 (M-H_2-^{t}BuMe$_2$SiO)$^+$, 293 (M-$C_8H_{13}O_2$)$^+$, 259 ($C_{13}H_{27}O_3Si$)$^+$, 227 ($C_{12}H_{23}O_2Si$)$^+$, 173 ($C_8H_{13}O_4$)$^+$, 159 ($C_8H_{15}O_3$)$^+$, 127

$(C_7H_{11}O_2)^+$, 115 $(C_6H_{11}O_2)^+$, 101 $(C_5H_9O_2)^+$, and 89 $(C_4H_9O_2)^+$, (Observed (M-H)$^+$, 433.2622, calc for $C_{21}H_{41}O_7Si$ (M-H), 433.2621), (Found C, 57 62, H, 9 23, $C_{23}H_{44}O_4Si$ requires C, 58 03, H, 9 74%)

(3*RS*)-1,2:5,6-Di-*O*-isopropylidene-3-*O*-(tetrahydro-2-*H*-pyran-2-yl)-α-D-glucofuranose (40).- Reaction of tetrahydro-2-(phenylsulphonyl)-2*H*-pyran (2) (110 mg, 0 49 mmol) with 1,2:5,6-diisopropylidene-α-D-glucofuranose (128 mg, 0 49 mmol, 1 0 equiv), $MgBr_2.Et_2O$ (256 mg, 0 99 mmol, 2 0 equiv) and $NaHCO_3$ (55 mg, 0 65 mmol, 1 3 equiv.) in dry distilled THF (2 0 ml) under ultrasound conditions overnight, followed by standard work-up and chromatography (gradient elution, Et_2O petrol, 1 8 - 1 6), gave the acetal product 40 (88 mg, 0 26 mmol, 53%) as a colourless oil and a separable mixture of diastereoisomers (*ca* 1 1) Diastereoisomer of higher Rf. ν_{max} (film) 2936, 1371, 1215, 1165, 1072 and 1022 cm^{-1}, δ_H (500 MHz) 1 31, 1 33, 1 41, and 1 50 (4 x 3H, 4 x s, 2 x CMe_2), 1 42-1 61 (4H, m, 4'-H_2 5'-H_2), 1 70-1 75 (1H, m, 3'-Hax), 1 78-1 82 (1H, m, 3'-Heq), 3 53-3 58 (1H, m, 6'-H), 3 87-3 92 (1H, m, 6'-H), 3 98 (1H, dd, *J* 8 5 6 0 Hz, 6-H), 4 09 (1H, dd, *J* 8 5 6 0 Hz, 6-H), 4 11 (1H, dd, *J* 8 0 3 0 Hz, 4-H), 4 21 (1H, d, *J* 2 5 Hz, 3-H), 4 23 (1H, dt, *J* 8 0 6 0 Hz, 5-H), 4 71 (1H, d, *J* 3 5 Hz, 2-H), 4 76 (1H, dd, *J* 5 0 2 5 Hz, 2'-H), 5 90 (1H, d, *J* 3 5 Hz, 1-H); m/z 344 (M)$^+$, 329 (M-CH_3)$^+$, 286 (M-$(CH_3)_2CO$)$^+$, 259 (M-C_5H_9O)$^+$, 243 (M-$C_5H_9O_2$)$^+$, 201 $(C_9H_{13}O_5)^+$, 186 $(C_9H_{14}O_4)^+$, 143 $(C_7H_{11}O_3)^+$, 129 $(C_6H_9O_3)^+$, 113 $(C_6H_9O_2)^+$, 101 $(C_5H_9O_2)^+$, and 85 $(C_5H_9O)^+$, (Found C, 59 12, H, 8 33, $C_{17}H_{28}O_7$ requires C, 59 29, H, 8 19%) Diastereoisomer of lower Rf ν_{max} (film) 2983, 2937, 1371, 1218, 1165, 1123, 1076, 1031, 972, 868, 850 and 815 cm^{-1}, δ_H (500 MHz) 1 30, 1 35, 1 43, and 1 50 (4 x 3H, 4 x s, 2 x CMe_2), 1 47-1 66 (4H, m, 4'-H_2 5'-H_2), 1 67-1 86 (2H, m, 3'-H_2), 3 48-3 53 (1H, m, 6'-Heq), 3 84 (1H, dd, *J* 11 0 6 5 Hz, 6'-Hax), 4 00 (1H, dd, *J* 8 5 6 5 Hz, 6-H), 4 13 (1H, dd, *J* 8 5 6 5 Hz, 6-H), 4 25 (1H, dd, *J* 7 0 3 0 Hz, 4-H), 4 35 (1H, d, *J* 3 5 Hz, 3-H), 4 43 (1H, q, *J* 6 5 Hz, 5-H), 4 49 (1H, d, *J* 3 5 Hz, 2-H), 4 71 (1H, t, *J* 2 5 Hz, 2'-H), 5 89 (1H, d, *J* 4 0 Hz, 1-H), m/z 344 (M)$^+$, 329 (M-CH_3)$^+$, 286 (M-$(CH_3)_2CO$)$^+$, 243 (M-$C_5H_9O_2$)$^+$, 229 (M-$C_6H_{11}O_2$)$^+$, 142 $(C_7H_{10}O_3)^+$, 129 $(C_6H_9O_3)^+$, 113 $(C_6H_9O_2)^+$, 101 $(C_5H_9O_2)^+$, and 85 $(C_5H_9O)^+$, (Found C, 59 23, H, 8 23, $C_{17}H_{28}O_7$ requires C, 59 29, H, 8 19%)

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