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Diastereoselective Synthesis of α,α'-Disubstituted Oxygen Heterocycles†

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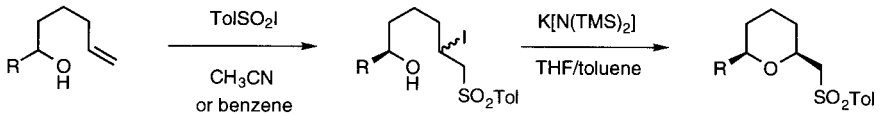
Abstract: Treatment of the *para*-toluenesulfonyl iodide adducts of a series of 1-substituted 5-hexenols with $K[N(TMS)_2]$ gave 2,6-disubstituted tetrahydropyrans with excellent *cis*-diastereoselectivity. The corresponding pentenols gave the 2,5-disubstituted tetrahydrofurans as 1:1 *cis:trans* mixtures.

Reliable diastereoselective syntheses of oxygen heterocycles are of fundamental importance for the preparation of natural products such as the annonaceous acetogenins;[1] these fascinating compounds usually contain tetrahydrofuran rings, but structures with pyranoid rings have also been reported.[2] The most widely exploited method for the preparation of oxacycles involves closure of the ring by formation of a C–O bond. Alkenols are popular precursors, and important methods for their cyclisation include the Bartlett iodocyclisation,[3] phenylselenation,[4] oxymercuration,[5] and acid-catalysed cyclisation of (alkene-derived) hydroxy epoxides.[6] An alternative approach involves a two step procedure namely, radical iodosulfonylation of an alkenol and subsequent cyclisation of the adduct on treatment with base to give a 2-substituted heterocycle.[7] In principle, a suitably placed substituent will lead to a general diastereoselective synthesis of "cyclosulfonylated" products. This work will show that the reaction proceeds smoothly to give oxygen heterocycles in most cases, and that excellent diastereoselectivity can be obtained in the formation of tetrahydropyrans.

For the synthesis of tetrahydropyrans, addition of *para*-toluenesulfonyl iodide to alkenols (**1** to **6**) in either acetonitrile or benzene gave the required β-iodosulfones (**7** to **12**) in excellent yields but with poor diastereoselectivity. Some minor unidentified impurities were observed by ^1H n.m.r. spectroscopy, however as it has been previously noted that β-iodosulfones are only moderately stable and do not survive chromatography intact,[7,8] the cyclisation step was effected on the crude products. Treatment of the parent iodosulfone (**7**) with either NaH or $Na[N(TMS)_2]$ in THF gave the pyran (**13**) in 50% and 56% yields respectively. Changing the base to $K[N(TMS)_2]$ and addition of toluene to the reaction solvent (THF:toluene ratio 1:3 v/v) resulted in an 87% yield of heterocycle (**13**). Application of these optimised reaction conditions to iodosulfones (**8** to **10**) gave the heterocycles (**14** to **16**) in variable yields with excellent diastereoselectivity

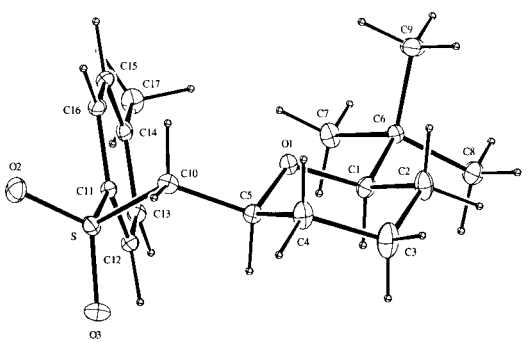
† The authors wish to dedicate this paper to the memory of Professor Paul Dowd (1936-1996).

(*cis*:*trans* ratio ≥50:1; overall yields are relative to the starting alkenol). These conditions do not seem applicable to the cyclohexyl (**11**) and phenyl (**12**) cases, where only complex mixtures were obtained. However cyclisation of the phenyl compound (**12**) to give heterocycle (**17**) can be effected using NaH as base in the second step.[9]



(**1**)	R = H	(**7**)	R = H	(**13**) R = H	86%	
(**2**)	R = Et	(**8**)	R = Et	(**14**) R = Et	52%	*d.r.* ≥50:1
(**3**)	R = Pr^i	(**9**)	R = Pr^i	(**15**) R = Pr^i	60%	*d.r.* ≥50:1
(**4**)	R = Bu^t	(**10**)	R = Bu^t	(**16**) R = Bu^t	36%	*d.r.* ≥50:1
(**5**)	R = *c*-C_6H_{11}	(**11**)	R = *c*-C_6H_{11}			
(**6**)	R = Ph	(**12**)	R = Ph	(**17**) R = Ph		

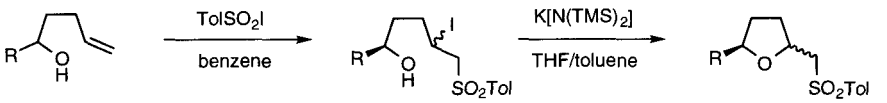
The *cis* relationship between the two substituents could generally be established using ^{1}H n.m.r. spectroscopy. Measurement of large axial-axial coupling constants between the axial H5 and the axial H6 (≈11 Hz) indicated that the alkyl group on C6 is equatorial (assuming a chair-like conformation of the heterocycle). While H2 was usually observed as a complex multiplet, its couplings to the diastereotopic CH_aS and CH_bS could be measured. If a first-order spectrum is assumed, then standard axial-axial (10.5 Hz), axial-equatorial (4.0 Hz), and equatorial-equatorial (3.5 Hz) couplings could be used to estimate the expected width of the n.m.r. signal.[10] These values were generally in good agreement with the width of the signals measured at half-height. For instance, with compound (**16**), $W_{1/2}$ = 25.5 Hz would be expected for an axial H2, but only 18.5 Hz for an equatorial H2; the observed value is 24.6 Hz, and therefore the substituent is equatorial. In a representative example, isolation of the major isomer of compound (**16**) and X-ray analysis (Figure) confirmed both the chair conformation of the six membered ring, and the *cis*-stereochemistry.[11] Bond lengths, and bond and torsional angles, are given in Tables 1 to 3, in the experimental section.



FIGURE

It has previously been communicated that cyclisation using the relatively weakly basic potassium carbonate in methanol leads to poor diastereoselectivity (*cis:trans* ratio ≈2:3) in the cyclisation of β-iodosulfone (**12**);[9] likewise, cyclisation of the *t*-butyl substituted alkenol (**10**) under these conditions proceeds to give a 2:1 mixture of diastereoisomers favouring the *trans* isomer.

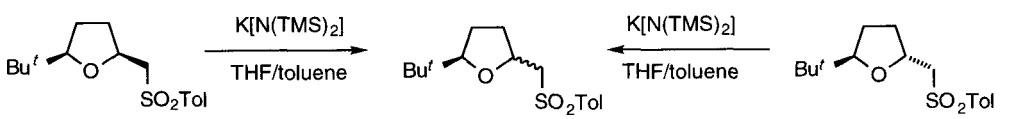
Extension of this procedure to the synthesis of tetrahydrofurans was less satisfactory. While addition of *para*-toluenesulfonyl iodide to two pentenols (**18** and **19**) occurred without incident giving β-iodosulfones (**20** and **21**), cyclisation gave the 2,5-disubstituted tetrahydrofurans (**22** and **23**) in 54% and 45% yields respectively (45% and 43% from the pentenols), and with a *cis:trans* ratio approaching 1:1.



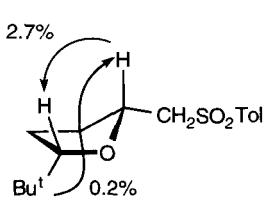
(**18**) R = Bu^t (**20**) R = Bu^t (**22**) R = Bu^t 45% d.r. ≈1:1

(**19**) R = *c*-C_6H_{11} (**21**) R = *c*-C_6H_{11} (**23**) R = *c*-C_6H_{11} 43% d.r. ≈2:3

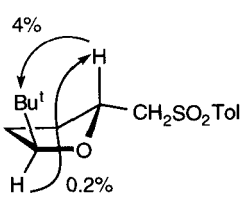
Careful chromatography gave small samples of the two *t*-butyl substituted tetrahydrofurans (**22C**) and (**22T**), the structures of which were readily established by the observation of enhancements in the nuclear Overhauser experiment: irradiation of H2 gave a 2.7% enhancement of H6 for the *cis* isomer (**22C**) and only a 0.2% enhancement for the *trans* isomer (**22T**). Similarly, irradiation of the *t*-butyl group leads to a 4% enhancement of H2 for the *trans* isomer and only a 0.2% enhancement for the *cis* isomer. Each of the constituent isomers (**22C** and **22T**) was treated in turn with K[N(TMS)$_2$] leading to the isolation of 1:1 mixtures, presumably as a result of equilibration *via* an acyclic vinyl sulfone. We are currently extending this procedure to the synthesis of other substituted tetrahydropyrans, as well as investigating alkylations using the sulfonyl group.



(**22C**) (**22**) d.r. ≈ 1:1 (**22T**)



Key nOe measurements for **22C** and **22T**



EXPERIMENTAL

General procedures and instrumentation have been described previously.[12] 5-Hexen-1-ol and 4-penten-1-ol were obtained from the Aldrich Chemical Company, and were used without further purification. Alkenols (**2**),[13] (**3**),[14] (**4**),[15] (**5**),[16] (**6**),[17] (**18**),[18] and (**19**)[16] were prepared by Swern oxidation[19] of either 5-hexen-1-ol or 4-penten-1-ol, and subsequent addition of the appropriate Grignard reagent to the intermediate aldehyde. A representative procedure is given below. The preparation of *para*-toluenesulfonyl iodide has been described previously.[12]

PROCEDURES

1-Cyclohexyl-5-hexen-1-ol (5)

A solution of 5-hexenal (0.80 g, 8.2 mmol) in dry diethyl ether (10 ml) was added at 0 °C to a solution of cyclohexyl magnesium chloride (prepared by dilution of 5 ml of a 2.0 M solution in diethyl ether, Aldrich reagent, 10.0 mmol, with a further 30 ml of dry ether) over 10 minutes and under an argon atmosphere. The reaction mixture was then heated under reflux for 2.5 hours, cooled and then hydrolysed by the addition of saturated aqueous ammonium chloride. The organic layer was separated, washed with brine and dried ($MgSO_4$), and the solvent was removed under reduced pressure yielding a colourless oil which was purified by flash chromtography (20% ether / light petroleum) followed by Kugelrohr distillation (110 °C / 0.4 mmHg) to give the title compound (**5**)[16] as a colourless oil (1.05 g, 70%), (Found: C, 78.7; H, 12.2. $C_{12}H_{22}O$ requires C, 79.1; H, 12.2%). ν_{max}(neat) 3350, 3080, 2920, 2870, 1640, 1450, 1410, 1100, 1065, 1030, 990, 965, 910, 890 cm^{-1}. δ_H(300MHz, $CDCl_3$) 0.90-1.93, m, 16H, aliphatic H, OH; 1.95-2.18, m, CH_2C=C; 3.30-3.34, m, 1H, C**H**OH; 4.90-5.05, m, 2H, C=CH_2; 5.79, ddt, *J* 16.9, 10.3, 6.7 Hz, 1H, CH=C. δ_C(75.5 MHz, $CDCl_3$) 25.1, 26.2, 26.3, 26.5, 27.7, 29.2, 33.5, 33.7 (signals from 25.1 to 33.7 are all CH_2), 43.6 (CH), 75.9 (CHOH), 114.4 (C=**C**H_2), 138.7 (C=**C**H). *m/z* 182 (M, <1%), 139 (39), 135 (11), 126 (18), 121 (10), 113 (35), 111 (35), 109 (10), 99 (59), 95 (100).

5-Iodo-6-(*para*-toluenesulfonyl)hexan-1-ol (7)

A solution of 5-hexen-1-ol (**1**) (250 mg, 2.5 mmol) and *para*-toluenesulfonyl iodide (705 mg, 2.5 mmol) in dry acetonitrile (25 ml) was stirred under an argon atmosphere, with the exclusion of light and at room temperature overnight. The solvent was removed under reduced pressure, and the residue was taken up in dichloromethane and washed successively with aqueous sodium thiosulfate and then water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave the *title compound* (**7**)[7] as a white solid (950 mg, 99%), m.p. 94-95 °C (Found: C, 41.0; H, 5.3. $C_{13}H_{19}IO_3S$ requires C, 40.85; H, 5.0%). ν_{max}(paraffin) 3550, 1305, 1295, 1265, 1150, 1140, 1120, 1085, 1065, 1045, 1020, 940, 825, 750, 740, 680 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 1.43-1.71, m, 5H, H3, H4 and OH; 1.82-2.12, m, 2H, H2; 2.47, s, 3H, $ArCH_3$; 3.67, q, *J* 5.6 Hz, 2H, C**H**$_2$OH; 3.71, dd, *J* 14.4, 9.2 Hz, 1H, CH_aS; 3.78, dd, *J* 14.4, 5.1 Hz, 1H, CH_bS; 4.43-4.53, m, 1H, CHI; 7.38, d, *J* 8.2 Hz, 2H, ArH; 7.78, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.7 ($ArCH_3$), 21.9 (CHI), 25.5 (CH_2), 31.4 (CH_2), 38.6 (CH_2), 62.3 (CH_2S), 65.6 (CH_2OH), 128.0 (ArCH), 130.2 (ArCH), 136.3 (Ar), 145.3 (Ar). *m/z* 383 (M+H, 2%), 255 (M–I, 31), 237 [M–(I+H_2O), 5], 227 (15), 209 (10), 158 (10), 157 (91), 155 (30), 139 (90), 97 (25), 92 (47), 91 (100).

7-Iodo-8-(*para*-toluenesulfonyl)octan-3-ol (8)

A solution of 7-octen-3-ol (**2**) (500 mg, 3.91 mmol) and *para*-toluenesulfonyl iodide (1.10 g, 3.90 mmol) in dry benzene (50 ml) was stirred under an argon atmosphere, with the exclusion of light and at room temperature overnight. The reaction was quenched by the addition of aqueous sodium thiosulfate (5% w/v), and the organic layer was removed, washed with water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave the *title compound* (**8**) as a viscous colourless oil (1.52 g, 95%), as a mixture of two diastereoisomers (3:1) (Found: C, 44.25; H, 5.9. $C_{15}H_{23}IO_3S$ requires C, 43.9; H, 5.65%). ν_{max}(neat) 3520, 3410, 2960, 2930, 2870, 1595, 1450, 1400, 1310, 1300, 1285, 1250, 1140, 1080, 810, 750, 730, 670 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.94 & 0.96, 2 x t (3:1), *J* 7.4 Hz, 3H, CH_3; 1.34-1.76, m, 7H, H2, H5, H6 and OH; 1.76-2.10, m, 2H, H4; 2.45, s, 3H, $ArCH_3$; 3.47-3.57, m, 1H, C**H**OH; 3.65-3.80, m, 2H, CH_2S; 4.39-4.53, m, 1H, CHI; 7.37, d, *J* 8.2 Hz, 2H, ArH; 7.78, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 9.8 & 9.9 (**C**H_3CH_2), 21.7 ($ArCH_3$), 22.0 (CHI), 25.1 & 25.7 (CH_2), 30.2 (CH_2), 35.4 & 35.5 (CH_2), 38.5 & 39.0 (CH_2), 65.4 & 65.7 (CH_2S), 72.5 & 72.9 (CHOH), 127.9 (ArCH), 130.1 (ArCH), 136.2 (Ar), 145.3 (Ar). *m/z* 411 (M+H, <1%), 393 (M–OH, 1), 381 (M–C_2H_5, 1), 283 (M–I, 5), 225 (14), 157 (55), 139 (26), 109 (78), 92 (28), 91 (100).

7-Iodo-2-methyl-8-(*para*-toluenesulfonyl)octan-3-ol (9)

This product, prepared from 2-methyl-7-octen-3-ol (**3**) by the general procedure described for iodosulfone (**8**), was isolated as a viscous yellow oil that eventually solidified to give the *title compound* (**9**) as a yellow solid (91%), as a mixture of two diastereoisomers (3:1), m.p. 42-43 °C (Found: C, 45.3; H, 6.0. $C_{16}H_{25}IO_3S$ requires C, 45.3; H, 5.9%). ν_{max}(neat) 3540, 2960, 2930, 2880, 1595, 1455, 1400, 1385, 1365, 1315, 1290, 1255, 1140, 1080, 1015, 975, 815, 755, 735, 675, 630 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.90 & 0.91, 2 x d (3:1), *J* 6.8 Hz, 6H, $C(CH_3)_2$; 1.28-1.77, m, 6H, C**H**$(CH_3)_2$, H5, H6, OH; 1.80-2.11, m, 2H, H4; 2.46, s, 3H, $ArCH_3$; 3.32-3.41, m, 1H, C**H**OH; 3.65-3.81, m, 2H, CH_2S; 4.40-4.53, m, 1H, CHI; 7.38, d, *J* 8.2 Hz, 2H, ArH; 7.79, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 17.0 & 17.3 [$C(\underline{C}H_3)_a$], 18.8 [$C(\underline{C}H_3)_b$], 21.6 ($ArCH_3$), 22.0 (CHI), 25.5 & 26.1 (CH_2), 32.7 & 32.9 (CH_2), 33.6 & 33.7 (CH), 38.6 & 39.2 (CH_2), 65.5 & 65.7 (CH_2S), 76.0 & 76.4 (CHOH), 128.0 (ArCH), 130.1 (ArCH), 136.2 (Ar), 145.3 (Ar). *m/z* 423 (M–H, <1%), 407 (M–OH, 1), 381 (M–C_3H_7, 5), 297 (M–I, 5), 225 (27), 157 (87), 139 (39), 123 (85), 97 (19), 92 (31), 91 (100).

7-Iodo-2,2-dimethyl-8-(*para*-toluenesulfonyl)octan-3-ol (10)

This product, prepared from 2,2-dimethyl-7-octen-3-ol (**4**) by the general procedure described for iodosulfone (**7**), was isolated as a viscous yellow oil that eventually solidified to give the *title compound* (**10**) as a yellow solid (94%), as a mixture of two diastereoisomers (1:1), m.p. 51-55 °C (Found: C, 46.65; H, 6.2. $C_{17}H_{27}IO_3S$ requires C, 46.6; H, 6.2%). ν_{max}(neat) 3560, 3530, 2940, 2860, 1455, 1375, 1360, 1315, 1300, 1265, 1160, 1130, 1080, 810, 760, 740, 620 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.90 & 0.91, 2 x s (1:1), 9H, $C(CH_3)_3$; 1.15-1.71, m, 5H, H5, H6, and OH; 1.74-2.12, m, 2H, H4; 2.46, s, 3H, $ArCH_3$; 3.20, t, *J* 9.9 Hz, 1H, C**H**OH; 3.72-3.78, m, 2H, CH_2S; 4.41-4.53, m, 1H, CHI; 7.37, d, *J* 8.2 Hz, 2H, ArH; 7.78, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.7 ($ArCH_3$), 22.0 & 22.1 (CHI), 25.7 [$C(\underline{C}H_3)_3$], 26.4 & 27.1 (CH_2), 30.0 & 30.3 (CH_2), 34.9 & 35.0 [$\underline{C}(CH_3)_3$], 38.5 & 39.2 (CH_2), 65.5 & 65.7 (CH_2S), 79.1 & 79.8 (CHOH), 128.0 (ArCH), 130.1 (ArCH), 136.4 (Ar), 145.3 (Ar). *m/z* 438 (M, 1%), 423 (M–CH_3, 2), 422 (5), 421 (M–OH, 29), 381 (M–

C_4H_9, 20), 311 (M–I, 12), 293 [M–(I+H_2O), 35], 225 (21), 157 (45), 139 (35), 138 (20), 137 (100), 97 (20), 95 (16), 92 (21), 91 (60).

1-Cyclohexyl-5-iodo-6-(*para*-toluenesulfonyl)hexan-1-ol (11)

This product, prepared from 1-cyclohexyl-5-hexen-1-ol (**5**) by the general procedure described for iodosulfone (**7**), was isolated as a viscous yellow oil that eventually solidified to give the *title compound* (**11**) as a yellow solid (96%), as a mixture of two diastereoisomers (1:1), m.p. 48-49 °C (Found: C, 49.1; H, 6.4. $C_{19}H_{29}IO_3S$ requires C, 49.1; H, 6.3%). ν_{max}(neat) 3530, 2920, 2850, 1595, 1445, 1400, 1315, 1300, 1260, 1180, 1140, 1080, 1060, 1040, 1015, 810, 755, 735, 670, 625 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.92-2.10, m, 18H, aliphatic H, OH; 2.46, s, 3H, $ArCH_3$; 3.31-3.39, m, 1H, C**H**OH; 3.70-3.77, m, 2H, CH_2S; 4.39-4.51, m, 1H, CHI; 7.37, d, *J* 8.2 Hz, 2H, ArH; 7.78, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.7 ($ArCH_3$), 22.1 (CHI), 25.4, 26.0, 26.1, 26.3, 26.5, 27.7, 27.9, 29.2, 32.7, 32.8, 38.6, 39.2 (signals from 25.4 to 39.2 are all CH_2; both isomers), 43.7 & 43.8 (ring CH), 65.6 & 65.8 (CH_2S), 75.4 & 75.9 (CHOH), 128.0 (ArCH), 130.1 (ArCH), 136.4 (Ar), 145.3 (Ar). *m/z* 463 (M–H, <1%), 447 (M–OH, 2), 381 (M–C_6H_{11}, 12), 225 (62), 196 (12), 163 (60), 157 (88), 139 (45), 121 (15), 97 (22), 95 (64), 91 (100).

5-Iodo-1-phenyl-6-(*para*-toluenesulfonyl)hexan-1-ol (12)

This product was prepared from 1-phenyl-5-hexen-1-ol (**6**) by the general procedure described for iodosulfone (**7**) except that the reaction required 3 days at room temperature for completion; the *title compound* (**12**)[9] was isolated as a viscous yellow oil (90%), as a mixture of two diastereoisomers (1:1), (Found: C, 49.5; H, 4.9. $C_{19}H_{23}IO_3S$ requires C, 49.8; H, 5.1%). ν_{max}(neat) 3500, 3060, 3030, 2930, 2860, 1595, 1450, 1400, 1300, 1140, 1080, 1040, 1015, 835, 815, 755, 735, 700, 670, 625 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 1.33-2.14, m, 7H, H2, H3, H4, and OH; 2.46, s, 3H, $ArCH_3$; 3.64-3.82, m, 2H, CH_2S; 4.36-4.51, m, 1H, CHI; 4.65-4.73, m, 1H, C**H**OH; 7.26-7.41, m, 7H, ArH; 7.77, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.7 ($ArCH_3$), 21.8 (CHI), 25.5 & 26.0 (CH_2), 37.7 (CH_2), 38.5 & 39.0 (CH_2), 65.6 & 65.8 (CH_2S), 73.9 & 74.3 (CHOH), 125.8 (PhCH), 127.6 & 127.7 (PhCH), 128.0 (ArCH), 128.4 & 128.5 (PhCH), 130.1 (ArCH), 136.3 (Ar), 144.4 (Ph), 145.3 (Ar). *m/z* 458 (M, <1%), 225 (17), 196 (35), 195 (25), 161 (15), 157 (19), 155 (44), 139 (16), 117 (13), 107 (57), 91 (100).

6-Iodo-2,2-dimethyl-7-(*para*-toluenesulfonyl)heptan-3-ol (20)

This product was prepared from 2,2-dimethyl-6-hepten-3-ol (**18**) by the general procedure described for iodosulfone (**8**); the *title compound* (**20**) was isolated as a viscous yellow oil (84%), as a mixture of two diastereoisomers (1:1), (Found: C, 45.6; H, 6.2. $C_{16}H_{25}IO_3S$ requires C, 45.3; H, 5.9%). ν_{max}(neat) 3530, 2960, 2870, 1595, 1480, 1445, 1400, 1365, 1315, 1300, 1290, 1185, 1140, 1080, 1015, 925, 905, 815, 735, 675 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.90 & 0.91, 2 x s, 9H, $C(CH_3)_3$, both isomers (ratio ≈ 1:1); 1.25-1.40, m, 1H, $H5_a$, both isomers; 1.40-1.53, m, 1H, $H5_b$, both isomers; 1.53-1.92, m, 1.5H, $H4_a$ for one isomer, OH for both isomers; 2.09, q, *J* 6.7 Hz, 1H, $H4_b$, both isomers; 2.28-2.40, m, 0.5H, $H4_a$, one isomer; 2.46, s, 3H, $ArCH_3$, both isomers; 3.20, td, *J* 10.0, 1.9 Hz, 1H, C**H**OH, both isomers; 3.66-3.73, m, 2H, CH_2S, both isomers; 4.43-4.56, m, 1H, CHI, both isomers; 7.38, d, *J* 8.2 Hz, 2H, ArH, both isomers; 7.79, d, *J* 8.2 Hz, 2H, ArH, both isomers. δ_C (75.5 MHz, $CDCl_3$) 21.7 ($ArCH_3$), 21.9 & 22.8 (CHI), 25.6 [$C(\underline{C}H_3)_3$], 31.0 & 31.3 (CH_2), 35.0 & 35.1 [$\underline{C}(CH_3)_3$], 36.5 & 37.5 (CH_2), 65.8 (CH_2S), 78.2 & 79.7 (CHOH), 128.1 (ArCH),

130.1 (ArCH), 136.4 (Ar), 145.3 (Ar). *m/z* 407 (M-OH, <1%), 367 (M–C_4H_9, 11), 297 (M–I, 5), 254 (23), 239 (17), 211 (29), 157 (44), 155 (26), 139 (35), 127 (19), 126 (34), 123 (57), 92 (27), 91 (100).

1-Cyclohexyl-4-iodo-5-(*para*-toluenesulfonyl)pentan-1-ol (21)

This product, prepared from 1-cyclohexyl-4-penten-1-ol (**19**) by the general procedure described for iodosulfone (**8**), was isolated as a viscous oil that eventually solidified to give the *title compound* (**21**) as a yellow solid (95%) as a mixture of two diastereoisomers (1:1), m.p. 61-72 °C (Found: C, 48.4; H, 6.15. $C_{18}H_{27}IO_3S$ requires C, 48.0; H, 6.0%). ν_{max}(neat) 3530, 3030, 2920, 2850, 1595, 1480, 1445, 1400, 1330, 1300, 1260, 1180, 1140, 1080, 1060, 1030, 1015, 810, 745, 735, 675 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.92-2.30, m, 16H, aliphatic H and OH; 2.46, s, 3H, $ArCH_3$; 3.33-3.40, m, 1H, C<u>H</u>OH; 3.66-3.82, m, 2H, CH_2S; 4.43-4.55, m, 1H, CHI; 7.38, d, *J* 8.2 Hz, 2H, ArH; 7.79, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.7 ($ArCH_3$), 22.0 & 22.6 (CHI), 26.1, 26.2, 26.3, 26.4, 26.5, 27.6, 28.0, 29.1, 29.2, 33.6, 35.6, 35.9 (signals from 26.1 to 35.9 are all CH_2; both isomers), 43.5 & 43.7 (CH), 65.6 & 65.7 (CH_2S), 74.7 & 75.6 (CHOH), 128.0 (ArCH), 130.1 (ArCH), 136.2 (Ar), 145.3 (Ar). *m/z* 433 (M-OH, 1%), 367 (M–C_6H_{11}, 7), 239 (33), 211 (34), 167 (11), 157 (22), 155 (37), 149 (65), 139 (25), 128 (11), 107 (11), 95 (39), 92 (34), 91 (100).

2-(*para*-Toluenesulfonyl)methyltetrahydropyran (13)

A solution of potassium hexamethyldisilazide ($K[N(TMS)_2]$; 7.5 ml of a 0.5 M solution in toluene, 3.75 mmol) was added dropwise to a solution of 5-iodo-6-(*para*-toluenesulfonyl)hexan-1-ol (**7**) (950 mg, 2.49 mmol) in dry toluene (40 ml) and dry THF (15 ml) under an atmosphere of argon and at 0 °C over 5 min. The resulting yellow solution was then stirred at room temperature for 2 h, cooled in ice and quenched with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water, dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a yellow oil. Purification by flash chromatography (60% ether / light petroleum) gave the title compound (**13**)[7] as a colourless crystalline solid (550 mg, 87%), m.p. 76-77 °C (Found: C, 61.6; H, 7.4. $C_{13}H_{18}O_3S$ requires C, 61.4; H, 7.1%). ν_{max}(paraffin) 1350, 1305, 1295, 1270, 1250, 1200, 1185, 1165, 1135, 1110, 1080, 1050, 1035, 805, 740, 655 cm^{-1}. δ_H(300 MHz, $CDCl_3$) 1.22-1.71, m, 5H, ring H; 1.71-1.87, m, 1H, ring H; 2.44, s, 3H, $ArCH_3$; 3.09, dd, *J* 14.5, 3.8 Hz, 1H, CH_aS; 3.27-3.40, m, 1H, $H6_a$; 3.33, dd, *J* 14.5, 7.7 Hz, 1H, CH_bS; 3.75-3.89, m, 2H, H2, $H6_b$; 7.33, d, *J* 8.2 Hz, 2H, ArH; 7.78, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.6 ($ArCH_3$), 23.1 (CH_2), 25.2 (CH_2), 31.5 (CH_2), 62.3 (CH_2S), 68.3 (OCH_2), 72.4 (OCH), 128.1 (ArCH), 129.6 (ArCH), 137.4 (Ar), 144.4 (Ar). *m/z* 255 (M+H, 10%), 155 (16), 105 (15), 98 (63), 92 (34), 91 (100).

6-Ethyl-2-(*para*-toluenesulfonyl)methyltetrahydropyran (14)

This product was prepared from 7-iodo-8-(*para*-toluenesulfonyl)octan-3-ol (**8**) as described in the method for (**13**) above (except that only 1.1 mol equiv of $K[N(TMS)_2]$ were used, and the reaction was stirred at room temp. overnight), and was purified by flash chromatography (40% ether / light petroleum) to give the *title compound* (**14**) as a colourless crystalline solid (55%), as a mixture (≥50:1) of two diastereoisomers [as determined by integration of triplets in the ^1H n.m.r. spectrum at δ 0.67 and 0.77 p.p.m., ratio ≥50:1] which could not be separated, m.p. 85 °C (Found: C, 63.7; H, 7.9. $C_{15}H_{22}O_3S$ requires C, 63.8; H, 7.85%). ν_{max}(paraffin) 1300, 1285, 1210, 1145 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.67, t, *J* 7.7 Hz, 3H, C<u>H</u>$_3CH_2$;

0.95-1.11, m, 1H, $H4_a$; 1.11-1.29, m, 3H, $H4_b$, $C\underline{H}_2CH_3$; 1.39-1.56, m, 2H, H5; 1.58-1.67, m, 1H, $H3_a$; 1.73-1.82, m, 1H, $H3_b$; 2.40, s, 3H, $ArCH_3$; 3.02-3.11, m, $W_{1/2}$ 25.5 Hz, 1H, H6; 3.10, dd, *J* 14.6, 3.8 Hz, 1H, CH_aS; 3.36, dd, *J* 14.6, 7.6 Hz, 1H, CH_bS; 3.77-3.87, m, $W_{1/2}$ 24.9 Hz, 1H, H2; 7.30, d, *J* 8.2 Hz, 2H, ArH; 7.77, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 9.4 ($\underline{C}H_3CH_2$), 21.5 ($ArCH_3$), 23.2 (CH_2), 28.7 (CH_2), 30.0 (CH_2), 31.3 (CH_2), 62.3 (CH_2S), 72.3 (OCH), 79.2 (OCH), 128.0 (ArCH), 129.5 (ArCH), 137.4 (Ar), 144.2 (Ar). *m/z* 283 (M+H, 9%), 254 (M-C_2H_6, 2), 157 (13), 155 (49), 139 (16), 127 (24), 126 (61), 97 (26), 91 (100).

6-(2-Propyl)-2-(*para*-toluenesulfonyl)methyltetrahydropyran (15)

This product was prepared from 7-iodo-2-methyl-8-(*para*-toluenesulfonyl)octan-3-ol (**9**) as described in the method for (**13**) above, and was purified by flash chromatography (50% ether / light petroleum) to give the *title compound* (**15**) as a colourless crystalline solid (66%), as a mixture (≥50:1) of two diastereoisomers [as determined by integration of signals in the ^1H n.m.r. spectrum at δ 0.68 and 0.77 p.p.m., ratio ≥50:1] which could not be separated, m.p. 99-100 °C (Found: C, 65.1; H, 8.3. $C_{16}H_{24}O_3S$ requires C, 64.8; H, 8.2%). ν_{max}(paraffin) 1295, 1280, 1265, 1250, 1140, 1120, 1085, 1060, 1040, 775 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.68 & 0.70, 2 x d, *J* 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$; 1.00-1.15, m, 1H, $H4_a$; 1.15-1.30, m, 1H, $H4_b$; 1.38-1.58, m, 3H, H5 & $C\underline{H}(CH_3)_2$; 1.63-1.70, m, 1H, $H3_a$; 1.78-1.88, m, 1H, $H3_b$; 2.43, s, 3H, $ArCH_3$; 2.90, ddd, *J* 11.0, 6.4, 1.8 Hz, 1H, H6; 3.13, dd, *J* 14.6, 3.8 Hz, 1H, CH_aS; 3.40, dd, *J* 14.6, 7.3 Hz, 1H, CH_bS; 3.80-3.88, m, $W_{1/2}$ 24.4 Hz, 1H, H2; 7.31, d, *J* 8.2 Hz, 2H, ArH; 7.78, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 17.9 & 18.4 ($C(\underline{C}H_3)_2$), 21.6 ($ArCH_3$), 23.3 (CH_2), 27.0 (CH_2), 31.5 (CH_2), 32.8 ($\underline{C}H(CH_3)_2$), 62.3 (CH_2S), 72.3 (OCH), 83.0 (OCH), 128.0 (ArCH), 129.6 (ArCH), 137.4 (Ar), 144.3 (Ar). *m/z* 297 (M+H, 10%), 254 (M-C_3H_6, 13), 253 (M-C_3H_7, 46), 157 (24), 155 (56), 141 (15), 140 (39), 139 (18), 97 (53), 91 (100).

6-(1,1-Dimethylethyl)-2-(*para*-toluenesulfonyl)methyltetrahydropyran (16)

This product was prepared from 7-iodo-2,2-dimethyl-8-(*para*-toluenesulfonyl)octan-3-ol (**10**) as described in the method for (**13**) above, and was purified by flash chromatography (40% ether / light petroleum) to give the *title compound* (**16**) as a colourless crystalline solid (38%), as a mixture (≥50:1) of two diastereisomers [as determined by integration of signals in the ^1H n.m.r. spectrum at δ 0.70 and 0.76 p.p.m., ratio ≥50:1] which could not be separated, m.p. 105 °C (Found: C, 66.0; H, 8.3. $C_{17}H_{26}O_3S$ requires C, 65.8; H, 8.4%). ν_{max}(paraffin) 1600, 1335, 1310, 1295, 1285, 1140, 1110, 1085, 1050, 1020, 780, 770 cm^{-1}. δ_H(300 MHz, $CDCl_3$) 0.70, s, 9H, $C(C\underline{H}_3)_3$; 1.08-1.31, m, 2H, H4; 1.49-1.56, m, 2H, H5; 1.63-1.72, m, 1H, $H3_a$; 1.81-1.90, m, 1H, $H3_b$; 2.43, s, 3H, $ArCH_3$; 2.83, dd, *J* 11.4, 1.7 Hz, 1H, H6; 3.12, dd, *J* 14.5, 4.4 Hz, 1H, CH_aS; 3.41, dd, *J* 14.5, 6.6 Hz, 1H, CH_bS; 3.78-3.84, m, $W_{1/2}$ 24.6 Hz, 1H, H2; 7.33, d, *J* 8.2 Hz, 2H, ArH; 7.79, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.5 ($ArCH_3$), 23.5 (CH_2), 24.6 ($\underline{C}H_2$), 25.8 ($C(\underline{C}H_3)_3$), 31.8 (CH_2), 33.9 ($\underline{C}(CH_3)_3$), 62.4 (CH_2S), 72.3 (OCH), 85.8 (OCH), 127.8 (ArCH), 129.7 (ArCH), 137.4 (Ar), 144.3 (Ar). *m/z* 311 (M+H, 2%), 253 (M-C_4H_9, 38), 157 (18), 155 (37), 154 (14), 139 (15), 97 (92), 91 (100).

6-Phenyl-2-(*para*-toluenesulfonyl)methyltetrahydropyran (17)

A suspension of anhydrous potassium carbonate (130 mg, 0.94 mmol) in a solution of 5-iodo-1-phenyl-6-(*para*-toluenesulfonyl)hexan-1-ol (**12**) (251 mg, 0.55 mmol) in dry methanol (5 ml) was stirred under an atmosphere of argon and at room temperature overnight. The suspension was then filtered and the solvent

evaporated to give a yellow solid that was purified by flash chromatography (60% ether / light petroleum) yielding the *title compound* (**17**)[9,20] as a colourless crystalline solid (95 mg, 52%), as a mixture of two diastereoisomers [as determined by integration of signals in the ^{1}H n.m.r. spectrum at δ_{cis} 2.29 and δ_{trans} 2.33 p.p.m., ratio ≈2:3] that could not be separated, m.p. 132-142 °C. A satisfactory microanalysis could not be obtained. $\nu_{max}(CH_2Cl_2)$ 1420, 1160, 1145, 905 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 1.48-1.62, m, 1H, H4$_a$, both isomers; 1.76-2.20, m, 5H, H3, H4$_b$ and H5, both isomers; 2.29 & 2.33, 2 x s, 3H, $ArCH_3$ *cis* and *trans*, ratio 2:3; 3.18-3.28, m, 1H, CH_aS, both isomers; 3.43-3.52, m, 1H, CH_bS*cis*; 3.71, dd, *J* 14.6, 7.4 Hz, 1H, CH_bS*trans*; 4.03-4.13, m, 1H, H2*cis*; 4.24, dd, *J* 11.3, 2.0 Hz, 1H, H6*cis*; 4.38-4.52, m, 2H, H2*trans* and H6*trans*; 6.93-7.00, m, 2H, ArH*cis*; 7.09, d, *J* 8.2 Hz, 2H, ArH*cis*; 7.13-7.41, m, 10H, ArH, both isomers; 7.70, d, *J* 8.2 Hz, 2H, ArH*cis*; 7.75, d, *J* 8.2 Hz, 2H, ArH*trans*. δ_C (75.5 MHz, $CDCl_3$) 18.8 (CH_2), 21.5 & 23.6 ($ArCH_3$), 29.2 (CH_2), 30.7 (CH_2), 31.1 (CH_2), 32.8 (CH_2), 58.5 & 62.3 (CH_2S), 67.4 (OCH), 72.7 (OCH), 73.1 (OCH), 79.6 (OCH), 125.6 (ArCH), 126.1 (ArCH), 127.1 (ArCH), 127.8 (ArCH), 128.1 (ArCH), 129.4 (ArCH), 129.6 (ArCH), 136.8 (Ar), 141.4 (Ar), 144.1 (Ar), 144.4 (Ar).

5-(1,1-Dimethylethyl)-2-(*para*-toluenesulfonyl)methyltetrahydrofuran (22)

This product was prepared from 6-iodo-2,2-dimethyl-7-(*para*-toluenesulfonyl)heptan-3-ol (**20**) as described in the method for (**13**) above, and was purified by flash chromatography (40% ether / light petroleum) to give the *title compound* (**22**) as a colourless crystalline solid (54%), as a mixture (≈1:1) of two diastereoisomers [as determined by integration of signals in the ^{1}H n.m.r. spectrum at δ 0.69 and 0.73 p.p.m., ratio ≈1:1] that could not be separated satisfactorily. Careful gravity chromatography led to the isolation of small amounts of each diastereoisomer which were identified using nuclear Overhauser effect measurements (see discussion above); the *cis* isomer (**22C**) eluted first and was isolated as a colourless crystalline solid, m.p. 92-94 °C (Found: C, 64.65; H, 8.1. $C_{16}H_{24}O_3S$ requires C, 64.8; H, 8.2%). ν_{max}(paraffin) 1360, 1295, 1285, 1140, 1080, 770, 625 cm^{-1}. δ_H (500 MHz, $CDCl_3$) 0.69, s, 9H, $C(CH_3)_3$; 1.47-1.78, m, 3H, ring H; 2.05-2.14, m, 1H, H3$_a$; 2.43, s, 3H, $ArCH_3$; 3.16, dd, *J* 14.2, 5.9 Hz, 1H, CH_aS; 3.38, dd, *J* 14.2, 6.4 Hz, 1H, CH_bS; 3.41, dd, *J* 8.2, 6.9 Hz, 1H, H5; 4.24, quintet, *J* 6.4 Hz, 1H, H2; 7.32, d, *J* 8.2 Hz, 2H, ArH; 7.79, d, *J* 8.2 Hz, 2H, ArH. δ_C(75.5 MHz, $CDCl_3$) 21.6 ($ArCH_3$), 25.5 [$C(\underline{C}H_3)_3$], 31.6 (CH_2 for C3, C4), 33.1 [$\underline{C}(CH_3)_3$], 61.8 (CH_2S), 72.9 (OCH), 87.9 (OCH), 128.3 (ArCH), 129.6 (ArCH), 137.1 (Ar), 144.4 (Ar). *m/z* 297 (M+H, 9%), 281 (M-CH_3, 3), 240 (M-C_4H_8, 16), 239 (M-C_4H_9, 79), 157 (34), 155 (61), 139 (29), 92 (20), 91 (100).

Further elution gave the *trans* diastereoisomer (**22T**) which was isolated as a colourless crystalline solid, m.p. 99-100 °C (Found: C, 65.2; H, 8.3. $C_{16}H_{24}O_3S$ requires C, 64.8; H, 8.2%). ν_{max}(paraffin) 1360, 1295, 1285, 1140, 1080, 770, 625 cm^{-1}. δ_H (500 MHz, $CDCl_3$) 0.73, s, 9H, $C(CH_3)_3$; 1.57-1.68, m, 2H, H4; 1.74-1.81, m, 1H, H3$_a$; 2.08-2.16, m, 1H, H3$_b$; 2.43, s, 3H, $ArCH_3$; 3.20, dd, *J* 14.3, 5.1 Hz, 1H, CH_aS; 3.40, dd, *J* 14.3, 6.9 Hz, 1H, CH_bS; 3.46, dd, *J* 9.0, 6.3 Hz, 1H, H5; 4.23-4.33, m, 1H, H2; 7.32, d, *J* 8.2 Hz, 2H, ArH; 7.81, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.6 ($ArCH_3$), 25.4 [$C(\underline{C}H_3)_3$], 26.6 (CH_2), 32.8 (CH_2), 33.9 [$\underline{C}(CH_3)_3$], 61.7 (CH_2S), 73.5 (OCH), 87.2 (OCH), 128.3 (ArCH), 129.6 (ArCH), 137.1 (Ar), 144.4 (Ar). *m/z* 297 (M+H, <1%), 281 (M-CH_3, <1), 240 (M-C_4H_8, 15), 239 (M-C_4H_9, 26), 157 (26), 155 (55), 139 (26), 92 (22), 91 (100).

5-Cyclohexyl-2-(*para*-toluenesulfonyl)methyltetrahydrofuran (23)

This product was prepared from 1-cyclohexyl-4-iodo-5-(*para*-toluenesulfonyl)pentan-1-ol (**21**) as described in the method for (**13**) above, and was purified by flash chromatography (60% ether / light petroleum) to give the *title compound* (**23**) as a colourless crystalline solid (45%), as a mixture (≈1.5:1) of two diastereoisomers [as determined by integration of signals in the ^{1}H n.m.r. spectrum at δ 3.10 and 3.11 p.p.m., ratio ≈1.5:1] that could not be separated, m.p. 124-126 °C (Found: C, 67.1; H, 8.0. $C_{18}H_{26}O_3S$ requires C, 67.05; H, 8.1%). ν_{max}(paraffin) 2700, 1300, 1285, 1140, 1085 cm^{-1}. δ_H (300 MHz, $CDCl_3$) 0.67-0.92, m, 2H, ring H; 1.01-1.31, m, 4H, ring H; 1.41-1.76, m, 7H, ring H; 1.80-1.96, m, 1H, $H3_a$; 2.00-2.22, m, 1H, $H3_b$; 2.44, s, 3H, $ArCH_3$; 3.10, dd, *J* 14.3, 5.9 Hz, and 3.11, dd, *J* 14.3, 5.6 Hz, 1H (ratio ≈ 1.5:1), CH_aS (both isomers); 3.34-3.52, m, 2H, H5, CH_bS; 4.19-4.34, m, 1H, H2; 7.33, d, *J* 8.2 Hz, 2H, ArH; 7.80, d, *J* 8.2 Hz, 2H, ArH. δ_C (75.5 MHz, $CDCl_3$) 21.6 ($ArCH_3$), 25.8, 26.0, 26.4, 28.2, 28.8, 29.0, 29.2, 29.4, 29.5, 31.3, 32.4 (signals from 25.8 to 32.4 are all CH_2; both isomers), 42.9 & 43.0 (CH), 61.6 & 61.9 (CH_2S), 72.6 & 72.7 (OCH), 83.5 & 84.4 (OCH), 128.2 (ArCH), 129.6 (ArCH), 137.2 (Ar), 144.4 (Ar). *m/z* 323 (M+H, 2%), 239 (M-C_6H_{11}, 44), 167 (19), 166 (19), 157 (43), 155 (84), 139 (45), 108 (25), 91 (100).

CRYSTALLOGRAPHY

Recrsytallisation of tetrahydropyran (**16**) from ether / light petroleum gave crystals suitable for analysis.

Crystal data. $C_{17}H_{26}O_3S$, M 310.5, monoclinic, space group $P2_1/c$, a 16.602(3), b 5.8417(7), c 24.132(4)Å, β 131.466(5)°, V 1753.8(5)Å^3, D_c 1.18 g cm^{-3}, Z 4, μ_{Cu} 16.54 cm^{-1}. Crystal size 0.14 by 0.18 by 0.28 mm, $2\theta_{max}$ 120°, min. and max. transmission factors 0.68 and 0.94. The number of reflexions was 1440 considered observed out of 2513 unique data, with R_{merge} 0.022 for 47 pairs of equivalent 0kl reflexions. Final residuals R, R_w were 0.057, 0.071 for the observed data.

Structure Determination. Reflexion data were measured with an Enraf-Nonius CAD-4 diffractometer in θ/2θ scan mode using nickel filtered copper radiation (λ 1.5418Å). Data were corrected for absorption using the analytical method of de Meulenaer and Tompa.[21] Reflexions with $I > 3\sigma(I)$ were considered observed. The structure was determined by direct phasing and Fourier methods. Hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full matrix least squares. Reflexion weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w=(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.[22] Structure solution was by MULTAN80[23] and refinement used BLOCKLS, a local version of ORFLS.[24] ORTEP-II[25] running on a Macintosh IIcx was used for the structural diagram, and a DEC Alpha-AXP workstation was used for calculations.

Table 1. Bond lengths (Å) for compound (**16**). Esd in parentheses.

O1–C1	1.385 (5)	C10–S	1.775 (5)	C1–C2	1.544 (7)
S–O2	1.436 (4)	C2–C3	1.541 (8)	S–O3	1.414 (4)
C3–C4	1.493 (8)	S–C11	1.755 (5)	C4–C5	1.517 (7)
C11–C12	1.381 (6)	C5–O1	1.405 (5)	C12-C13	1.382 (7)
C1–C6	1.544 (7)	C13–C14	1.394 (7)	C6–C7	1.527 (7)
C14–C15	1.373 (7)	C6–C8	1.530 (7)	C15–C16	1.377 (7)
C6–C9	1.515 (7)	C16–C11	1.388 (6)	C5–C10	1.507 (6)
C14–C17	1.499 (7)				

Table 2. Bond angles (°) for compound (**16**). Esd in parentheses

O2–S–O3	117.9 (3)	C1–C6–C8	108.1 (4)	C10–S–O2	104.8 (3)
C1–C6–C9	113.0 (5)	O2–S–C11	107.9 (2)	C7–C6–C8	108.0 (4)
C10–S–O3	110.1 (3)	C7–C6–C9	109.5 (5)	O3–S–C11	108.2 (2)
C8–C6–C9	110.0 (5)	C10–S–C11	107.5 (2)	C5–C10–S	115.5 (4)
C5–O1–C1	115.2 (4)	S–C11-C12	120.3 (4)	O1–C1–C2	110.1 (4)
S–C11–C16	119.5 (4)	O1–C1–C6	110.4 (4)	C16–C11–C12	120.1 (4)
C2–C1–C6	113.4 (5)	C11–C12–C13	118.8 (5)	C1–C2–C3	108.5 (5)
C12–C13–C14	122.1 (5)	C2–C3–C4	110.5 (5)	C13–C14–C15	117.2 (5)
C3–C4–C5	109.7 (5)	C13–C14–C17	121.1 (5)	C4–C5–O1	111.3 (4)
C15–C14–C17	121.6 (5)	O1–C5–C10	109.1 (4)	C14–C15–C16	122.1 (5)
C4–C5–C10	111.4 (4)	C15–C16–C11	119.5 (5)	C1–C6–C7	108.2 (4)

Table 3. Torsional angles (°) for compound (**16**). Esd in parentheses

O2–S–C11–C12	-132.6 (4)	C3–C2–C1–C6	179.8 (5)
O3–S–C11–C12	-4.1 (4)	C1–O1–C5–C10	-177.4 (4)
C10–S–C11–C12	114.8 (4)	C3–C4–C5–C10	-176.7 (5)
C1–C2–C3–C4	-54.7 (8)	O1–C1–C6–C7	-51.4 (5)
C2–C3–C4–C5	54.2 (8)	O1–C1–C6–C8	-168.0 (4)
C3–C4–C5–O1	-54.7 (7)	O1–C1–C6–C9	70.0 (5)
C4–C5–O1–C1	59.3 (6)	C2–C1–C6–C7	-175.4 (5)
C5–O1–C1–C2	-59.8 (6)	C2–C1–C6–C8	68.0 (6)
O1–C1–C2–C3	55.7 (7)	C2–C1–C6–C9	-54.0 (6)
C5–O1–C1–C6	174.3 (4)		

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