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Aspects of the Chemistry of 4-Tributylstannyl-, 4-Trimethylsilyl- and 2-Phenylsulfinylallylstannanes

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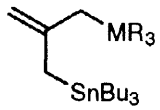
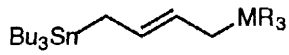
Abstract: The 4-trimethylsilyl- and 4-tributylstannylbut-2-enyl(tributyl)stannanes **3** and **4** have been prepared by treatment of the allylic sulfones **6** and **7** with tributyltin hydride under free-radical conditions and shown to react under non-catalysed and Lewis acid promoted conditions with 4-nitrobenzaldehyde to give the *anti*- and *syn*-products **9/11** and **8/10**, respectively, with reasonable levels of stereoselectivity. The 2-arylsulfinylpropenylstannanes **17** and **18** were also prepared from the sulfones **15** and **16**, and found to undergo stereoselective titanium(IV) chloride promoted reactions with aldehydes.

Allylstannanes are useful reagents for stereoselective organic synthesis.[1] Bis-metallated reagents are of interest at present and the 2-(tributylstannylmethyl)- and 2-(trimethylsilylmethyl)propenylstannanes **1** and **2** have been described in this respect.[2,3] Recently a synthesis of the 4-trimethylsilylbut-2-enyl(tributyl)stannane **3** was reported together with a study of its palladium(0) catalysed reactions with aryl iodides and aryl triflates.[4] We now describe an alternative synthesis of the 4-trimethylsilylbutenylstannane **3** and the corresponding bis-stannane **4** and the results of preliminary investigations into their reactions with aldehydes.[5,6] Of interest was the effect of the 4-substituent on the reactivity of these butenylstannanes. Syntheses of the 2-arylsulfinylpropenylstannanes **15** and **19** and the stereoselectivity of their reactions with aldehydes are also described.



1 $MR_3 = SnBu_3$
2 $MR_3 = SiMe_3$



3 $MR_3 = SiMe_3$
4 $MR_3 = SnBu_3$

RESULTS AND DISCUSSION

Regioselective alkylation of the propenylsulfone **5** using iodomethyl(trimethyl)silane[7] and iodomethyl-(tributyl)stannane[8] gave the α-alkylated sulfones **6** and **7**. Treatment of these sulfones with tributyltin hydride under free-radical conditions[9] then gave the 4-trimethylsilyl- and 4-tributylstannylpropenylsulfones **3** and **4**.

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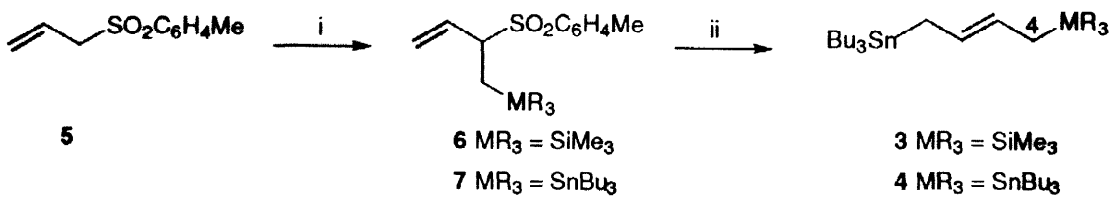

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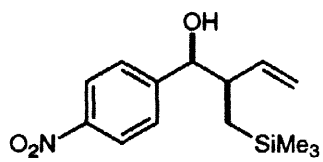
6 $MR_3 = SiMe_3$
7 $MR_3 = SnBu_3$

3 $MR_3 = SiMe_3$
4 $MR_3 = SnBu_3$

Scheme 1 ***Reagents and conditions:*** i, butyllithium, -78 °C, iodomethyl(trimethyl)silane or iodomethyl(tributyl)stannane (**6**, 49%; **7**, 30%); ii, tributyltin hydride, benzene, azoisobutyronitrile, heat under reflux (**3**, 92%, *E* : *Z* = 70 : 30; **4**, 47%, *E* : *Z* = 65 : 35).

Under non-catalysed conditions, the butenylstannanes **3** and **4** were found to be relatively unreactive towards aldehydes perhaps because of steric hindrance due to the 4-substituents. The reaction of the 4-trimethylsilylbut-2-enylstannane **3** with 4-nitrobenzaldehyde for example, which gave a mixture of the *syn*- and *anti*-alcohols **8** and **9** in which the *anti*-isomer **9** was the major component, **8** : **9** = 10 : 90 (62%), required heating in toluene in a sealed tube at 150 °C for 18 h.[5] Lewis acid promoted reactions, however, proceeded under mild conditions. For example, in the presence of boron trifluoride diethyletherate, the stannane **3** reacted with 4-nitrobenzaldehyde at -78 °C to give the *syn*-diastereoisomer **8** as the major product, **8** : **9** = 90 : 10 (65%).[6]



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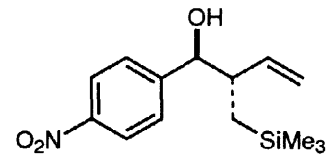

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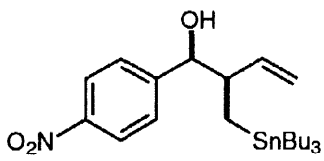
The structures **8** and **9** were assigned to these products on the basis of precedent[5,6] and spectroscopic data. The preferred formation of the *anti*-isomer **9** in the non-catalysed reactions is consistent with the *E*-isomer of the stannane **3** reacting with the aldehyde *via* a six-membered, chair-like, transition structure.[5] The *Z*-isomer which comprises about 30% of the stannane **3** would be expected to give the *syn*-diastereoisomer under these conditions[5] and so the increased preference for formation of the *anti*-isomer **9** may be due to *E*/*Z*-equilibration of the stannanes under the reaction conditions. The selectivity in favour of the *syn*-diastereoisomer **8** in the boron trifluoride diethyl etherate promoted reactions is consistent with the participation of open-chain processes which are known to give *syn*-isomers stereoselectively from both *E*- and *Z*-stannanes.[6]

Similar results were obtained using the 4-tributylstannylbut-2-enylstannane **4**. The *syn*-diastereoisomer **10** was the major product from boron trifluoride diethyl etherate promoted reactions with 4-nitrobenzaldehyde, **10** : **11** = 83 : 17 (77%), and the *anti*-isomer **11** was the major product from the non-catalysed reactions at 150 °C, **10** : **11** = 25 : 75 (21%). These hydroxystannanes may be useful for the stereoselective synthesis of cyclopropanes.[10]



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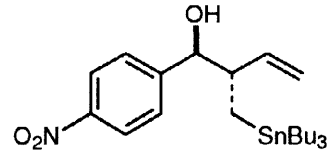

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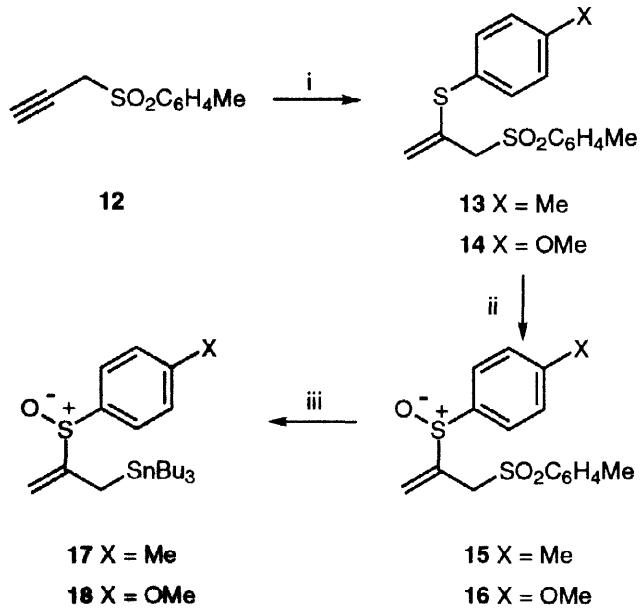
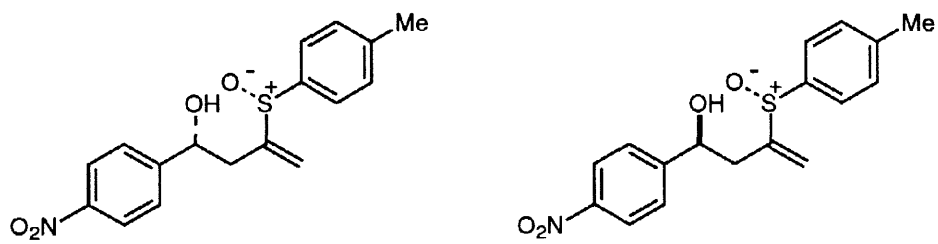
The 2-arylsulfinylpropenylstannanes **17** and **18** were prepared in order to assess the influence of the arylsulfinyl group on the reactivity and stereoselectivity of reactions of the allylstannanes with aldehydes. Thus addition of *p*-cresol and 4-methoxybenzenethiol to the propynyl sulfone **12** gave the vinyl thioethers **13**[11] and **14** which were converted into the 2-sulfinylpropenylstannanes **17** and **18** by oxidation to the sulfoxides **15** and **16** followed by treatment of the sulfoxides with tributyltin hydride under free-radical conditions.[9]



Scheme 2 ***Reagents and conditions*** i, *p*-thiocresol or 4-methoxybenzenethiol, triethylamine, benzene (**13**, 55%; **14**, 41%); ii, *m*-chloroperbenzoic acid, dichloromethane (**15**, 59%; **16**, 69%); iii, tributyltin hydride, azoisobutyronitrile, benzene, heat under reflux (**17**, 82%; **18**, 58%)

Reactions of the stannane **17** with 4-nitrobenzaldehyde in the presence of titanium(IV) chloride gave a mixture of the two stereoisomeric alkenols **19** and **20** (52%). The stereoselectivity of this reaction corresponded to a product ratio of 80 : 20 although the relative configurations of the products were not established. However, isomer **19** would be expected to be the major product if a chelated transition structure, *cf.* Figure 1, is involved.[12] Reactions between the propenylstannane **19** and 4-nitrobenzaldehyde were also carried out in the absence of catalyst by heating under reflux in toluene and gave a 55 : 45 mixture of products **19** and **20** (55%).



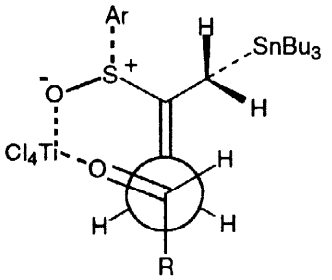
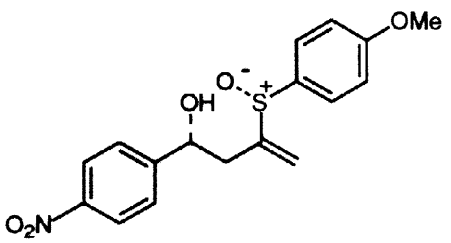


Figure 1

The reactivity of the (4-methoxyphenyl)sulfinylstannane **18** towards aldehydes was found to be very similar to that of the 4-methylphenyl analogue **15**. Thus reaction with 4-nitrobenzaldehyde, in the presence of an excess of titanium(IV) chloride, gave an 89 : 11 mixture of the diastereoisomeric alcohols **21** and **22**. If this reaction involves a chelated transition structure akin to that shown in Figure 1, the major product should correspond to isomer **21**. However this stereochemical assignment was not confirmed. Under uncatalysed conditions in toluene heated under reflux, a 55 : 45 mixture of the products **21** and **22** was obtained.



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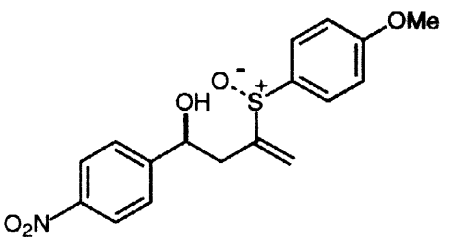

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CONCLUSIONS

This work shows that, unlike the 2-substituted propenylstannanes **1** and **2**, the 4-substituted compounds **3** and **4** show reduced reactivity towards aldehydes under non-catalysed conditions probably due to steric effects. Nevertheless, the *anti*-products can be obtained with more reactive aldehydes with useful stereoselectivity. Under Lewis acid catalysed conditions, the *syn*-products, e.g. **8** and **10**, are formed stereoselectively under mild conditions.

The 2-arylsulfinylpropenylstannanes **17** and **18** react with aldehydes with useful levels of 1,4-induction if the reactions are promoted by titanium(IV) chloride, but with only modest stereoselectivity under thermal conditions. Further work would study the stereocontrol of these reactions introduced by other Lewis acid catalysts, and establish the relative configurations of the products.

EXPERIMENTAL

All non-aqueous reactions were performed under an atmosphere of dry argon or nitrogen. Proton nuclear magnetic resonance spectra were recorded on Varian Unity 500 (500 MHz), Varian XL 300 (300 MHz), Bruker AC 300 (300 MHz) and Varian Gemini 200 (200 MHz) spectrometers in chloroform-d_1. Carbon nuclear magnetic

resonance spectra were recorded on a Varian Gemini 200 spectrometer. Infrared spectra were recorded on Perkin-Elmer 297 or 1710 FT spectrometers as evaporated films unless otherwise stated. Mass spectra were recorded on a Kratos Concept-1S spectrometer using electron impact (EI), chemical ionisation (CI) or field ionisation (FI) with peaks corresponding to ^{120}Sn being quoted.

Chromatography refers to flash column chromatography and was carried out using Merck silica gel 60H (40 - 63 μ, 230 - 300 mesh) or May and Baker Sorbsil C60 silica gel (40-60 μ) as the stationary phase. Light petroleum refers to the fraction which distils between 40 °C and 60 °C, ether refers to diethyl ether, and THF to tetrahydrofuran. All solvents were dried and distilled before use.

2-(4-Methylphenylsulfonyl)but-3-enyl(trimethyl)silane **6**

Butyllithium (1.6 M in hexane, 12.8 cm^3, 20.4 mmol) was added dropwise to a solution of the propenylsulfone **5** (4 g, 20.4 mmol) in THF (50 cm^3) under argon at -78 °C. Iodomethyl(trimethyl)silane (3.4 cm^3, 22.9 mmol) was added and the reaction mixture allowed to warm to room temperature then stirred for 0.5 h. Water (20 cm^3) was added, the mixture extracted with ether (50 cm^3), and the organic extracts dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the residue using ether-light petroleum (1:4) as eluent gave *title compound* **6** (2.84 g, 49%) as an oil (Found: C, 60.0; H, 8.15. $C_{14}H_{22}O_2SSi$ requires C, 59.6; H, 7.85%); υ_{max} 1630, 1590, 1400, 1310, 1240, 1140, 1080 and 840 cm^{-1}; δ_H -0.02 (9 H, s, $SiMe_3$), 0.93 (1 H, t, *J* 12.5, 1-H), 1.38 (1 H, dd, *J* 12.5, 2, 1-H'), 2.38 (3 H, s, Ar*Me*), 3.5 (1 H, m, 2-H), 4.90 - 5.20 (2 H, m, 4-H_2), 5.52 (1 H, dt, *J* 18, 8, 3-H) and 7.25 and 7.62 (each 2 H, d, *J* 9, ArH); *m/z* (CI) 300 (M^+ + 18, 80%), 270 (40) and 229 (100).

2-(4-Methylphenylsulfonyl)but-3-enyl(tributyl)stannane **7**

Butyllithium (1.6 M in hexane, 6 cm^3, 10.2 mmol) was added dropwise to a solution of the propenylsulfone **5** (2.0 g, 10.2 mmol) in THF (40 cm^3) under argon at -40 °C. Iodomethyl(tributyl)stannane (5.25 g, 12.2 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 3 h before being allowed to warmed to -10 °C. Water (20 cm^3) was added, the mixture extracted with ether (50 cm^3) and the organic extracts washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the residue using ether-light petroleum (1:6) as eluent gave the *title compound* **7** (1.5 g, 30%) as an oil; υ_{max} 1595, 1455, 1310, 1140, 1080 and 920 cm^{-1}; δ_H 0.7 - 1.6 (29 H, m, CH_2SnBu_3), 2.42 (3 H, s, Ar*Me*), 3.62 (1 H, m, 2-H), 4.92 - 5.25 (2 H, m, 4-H_2), 5.64 (1 H, dt, *J* 18, 8, 3-H) and 7.30 and 7.70 (each 2 H, d, *J* 9, ArH); *m/z* (FI) 500 (M^+).

4-Trimethylsilylbut-2-en-1-yl(tributyl)stannane **3**

Tributyltin hydride (1.02 g, 3.51 mmol) was added to a degassed solution of the sulfone **6** (0.50 g, 1.77 mmol) in benzene (5 cm^3) containing a trace of azoisobutyronitrile (AIBN) under an atmosphere of argon. The mixture was heated under reflux for 4 h and then concentrated under reduced pressure. Bulb to bulb distillation of the residue (bp 150 °C/0.15 mmHg) followed by flash chromatography using light petroleum as eluent gave the title compound **3** (680 mg, 92%) as a mixture of *E*- and *Z*-isomers, ratio *ca.* 2.5 : 1 (from ^{13}C NMR); υ_{max} 1590, 1480, 1030 and 850 cm^{-1}; δ_H 0.00 (9 H, s, $SiMe_3$), 0.9 (15 H, m), 1.2 - 1.75 (16 H, m) and 5.10 - 5.50 (2 H, m, 2-H and 3-H); *m/z* (FI) 418 (M^+); δ_C (major) -2.18, 8.82, 13.51, 13.95, 22.35, 27.22, 29.02, 121.46 and 127.63.

4-Tributylstannylbut-2-enyl(tributyl)stannane **4**

Tributyltin hydride (0.9 g, 3.1 mmol) was added to a degassed solution of the sulfone **7** (0.85 g, 1.7 mmol) in toluene (5 cm^3) containing a trace of AIBN under an atmosphere of argon. The reaction mixture was heated under reflux for 6 h and then concentrated under reduced pressure. Flash chromatography of the residue using light petroleum as eluent gave the *title compound* **4** (500 mg, 47%) as an oil, a mixture of *E*- and *Z*-isomers, ratio *ca.* 2:1 (from ^1H NMR); υ_{max} 1610, 1450, 1370, 1070 and 860 cm^{-1}; δ_H 0.8 - 1.65 (54 H, m, 2 x $SnBu_3$), 1.68 (4 H, m, 1-H_2 and 4-H_2), and 5.3 (2 H, m, 2-H and 3-H); *m/z* (FI) 636 (M^+); δ_C (major isomer) 8.82, 13.54, 13.73, 27.24, 28.88 and 124.70.

(1RS,2SR)-1-(4-Nitrophenyl)-2-trimethylsilylmethylbut-3-en-1-ol **8**

Boron trifluoride diethyletherate (0.1 cm^3, 0.8 mmol) was added to a solution of 4-nitrobenzaldehyde (50 mg, 0.33 mmol) and the stannanes **3** (300 mg, 0.72 mmol) in dichloromethane (2 cm^3) under an atmosphere of argon at -78 °C and the reaction mixture stirred at -78 °C for 4 h. Water (2 cm^3) was added and the resultant mixture extracted with dichloromethane. The organic extracts were washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the residue using ether-light petroleum (1:4) as eluent gave the *title compound* **8** (60 mg, 65%), mp 71 - 74 °C containing *ca.* 10% of the *anti*-diastereoisomer **9** (^1H NMR); υ_{max} ($CHCl_3$) 3600, 3020, 1610, 1520, 1350, 1250, 855 and 840 cm^{-1}; δ_H -0.05 (9 H, s, $SiMe_3$), 0.52 (1 H, dd, *J* 14, 12, 2-CH), 0.7 (1 H, dd, *J* 14, 2, 2-CH'), 2.25 (1 H, d, *J* 5, OH), 2.55 (1 H, m, 2-H), 4.70 (1 H, t, 5, 1-H), 5.08 (2 H, m, 4-H_2), 5.52 (1 H, dt, *J* 18, 8, 3-H) and 7.45 and 8.20 (each 2 H, d, *J* 9, ArH); *m/z* (CI) 297 (M^+ + 18, 50%) and 232 (25).

(1RS,2RS)-1-(4-Nitrophenyl)-2-trimethylsilylmethylbut-3-en-1-ol **9**

A solution of 4-nitrobenzaldehyde (35 mg, 0.23 mmol) and the butenylstannane **3** (190 mg, 0.46 mmol) in toluene (3 cm^3) was heated in a sealed tube at 150 °C for 18 h. After cooling and concentration under reduced pressure, flash chromatography of the residue using ether- light petroleum (1:4) as eluent gave the *title compound* **9** (40 mg, 62%) containing *ca.* 10% of its *syn*-diastereoisomer **8**, mp 72 - 74 °C (Found: $M^+ + NH_4$, 297.1641. $C_{14}H_{25}N_2O_3Si$ requires *M*, 297.1634); υ_{max} ($CHCl_3$) 3540, 3080, 3020, 1600, 1520, 1350, 1250 and 850 cm^{-1}; δ_H -0.05 (9 H, s, $SiMe_3$), 0.44 (1 H, dd, *J* 14, 4, 2-CH), 0.58 (1 H, dd, *J* 14, 12, 2-CH'), 2.4 (2 H, m, 2-H and OH), 4.45 (1 H, d, *J* 9, 1-H), 5.2 (2 H, m, 4-H_2), 5.62 (1 H, dt, *J* 18, 8, 3-H) and 7.52 and 8.22 (each 2 H, d, *J* 10, ArH); *m/z* (CI) 297 (M^+ + 18, 60%), 248 (40) and 232 (45).

(1RS, 2SR)-1-(4-nitrophenyl)-2-tributylstannylmethylbut-3-en-1-ol **10**

Boron trifluoride diethyletherate (0.08 cm^3, 0.64 mmol) was added to a mixture of 4-nitrobenzaldehyde (80 mg, 0.53 mmol) and the stannane **4** (400 mg, 0.63 mmol) in dichloromethane (5 cm^3) under argon at -78 °C and the mixture stirred at -78 °C for 2 h. Water (5 cm^3) was added and the mixture extracted with ether (25 cm^3). The organic extracts were washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the residue using ether-light petroleum (1:6) as eluent gave the *title compound* **10** (168 mg, 64%) as a pale yellow oil (Found: C, 55.95; H, 8.2; N, 2.6, $C_{23}H_{39}NO_3Sn$ requires C, 55.65; H, 7.9; N, 2.8%); υ_{max} 3400, 3080, 1600, 1520, 1460, 1350, 1040, 910 and 850 cm^{-1}; δ_H 0.6 - 1.7 (29 H, m, CH_2SnBu_3), 2.2 (1 H, d, *J* 5, OH), 2.6 (1 H, m, 2-H), 4.68 (1 H, t, *J* 5, 1-H), 5.05 (2 H, m, 4-H_2), 5.56 (1 H,

dt, *J* 18, 8 Hz, 3-H) and 7.48 and 8.20 (each 2 H, d, *J* 10, ArH); *m/z* (FI) 440 (M^+ - 57). Further elution gave the *anti*-diastereoisomer **11** (34 mg, 13%).

(1RS,2RS)-1-(4-nitrophenyl)-2-tributylstannylmethylbut-3-en-1-ol **11**

A solution of 4-nitrobenzaldehyde (40 mg, 0.26 mmol) and the stannane **4** (400 mg, 0.63 mmol) in toluene (1 cm^3) was heated in a sealed tube at 150 °C for 18 h. The reaction mixture was then cooled and concentrated under redu ed pressure. Flash chromatography of the residue using ether-light petroleum (1:8) as eluent gave the *title compound* **11** (21 mg, 16%) as a pale yellow oil (Found: C, 55.3; H, 7.9; N, 2.7. $C_{23}H_{39}NO_3Sn$ requires C, 55.65; H, 7.9; N, 2.8%); υ_{max} ($CHCl_3$) 3600, 1600, 1520, 1350 and 910 cm^{-1}; δ_H 0.6 - 1.5 (29 H, m, CH_2SnBu_3), 2.40 (1 H, d, *J* 2, OH), 2.48 (1 H, m, 2-H) 4.45 (1 H, dd, *J* 10, 2, 1-H), 5.2 (2 H, m, 4-H_2), 5.64 (1 H, dt, *J* 18, 8, 3-H) and 7.54 and 8.24 (each 2 H, d, *J* 10, ArH); *m/z* (FI) 497 (M^+).

3-(4-Methylphenylsulfonyl)-2-(4-methylphenylthio)propene **13**

p-Thiocresol (6.35 g, 51 mmol) was added to a solution of the sulfone **12** (8 g, 41 mmol) and triethylamine (0.5 cm^3, 3.6 mmol) in benzene (200 cm^3) uner argon. The reaction mixture was stirred at room temperature for 18 h, then washed with dilute aqueous sodium hydroxide, dilute aqueous hydrogen chloride, water and brine before being dried ($MgSO_4$) and concentrated under reduced pressure. Crystallisation of the residue from ether-hexane gave the title compound **13** (6.78 g, 55%) as white needles, mp 71 - 73 °C (lit.[11] 64-65 °C); υ_{max} 1597, 1493, 1087, 1034, and 886 cm^{-1}; δ_H 2.32 and 2.42 (each 3 H, s, ArCH_3), 3.85 (2 H, s, 3-H_2), 7.15 (4 H, s, ArH) and 7.30 and 7.75 (each 2 H, d, *J* 7, ArH); *m/z* (EI) 318 (M^+, 50%).

3-(4-Methylphenylsulfonyl)-2-(4-methoxyphenylthio)propene **14**

4-Methoxybenzenethiol (5.0 g, 35.7 mmol) was added to a solution of the sulfone **12** (7 g, 36 mmol) and triethylamine (1.0 cm^3, 7.2 mmol) in benzene (200 cm^3) under argon. The reaction mixture was stirred at room temperature for 18 h, then washed with dilute aqueous sodium hydroxide, dilute aqueous hydrogen chloride, water and brine before being dried ($MgSO_4$) and concentrated under reduced pressure. Crystallisaton of the residue from dichloromethane-hexane gave the *title compound* **14** (5.0 g, 41%) as white needles, mp 62 - 64 °C (Found: M^+, 334.0706. $C_{17}H_{18}O_2O_3$ requires *M*, 334.0697); υ_{max} 1719, 1593, 1494, 1320, 1291, 1250, 1174, 1147, 1106, 1086, 1029 and 830 cm^{-1}; δ_H 2.44 (3 H, s, ArCH_3), 3.81 (3 H, s, OCH_3), 3.87 (2 H, s, 3-H_2), 4.92 and 5.26 (each 1 H, s, 1-H), 6.84 and 7.21 (each 2 H, d, *J* 8, ArH) and 7.36 and 7.77 (each 2 H, d, *J* 7, ArH); *m/z* (EI) 334 (M^+, 20%) and 270 (5).

3-(4-Methylphenylsulfonyl)-2-(4-methylphenylsulfinyl)propene **15**

A solution of *m*-chloroperbenzoic acid (1.95 g, 11.3 mmol) in dichloromethane (50 cm^3) was added dropwise to a solution of the sulfide **13** (3 g, 9.4 mmol) in dichloromethane (150 cm^3) under argon at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and allowed to warm to -40 °C over 1 h, before being poured onto a mixture of ether (500 cm^3) and water (500 cm^3). The organic layer was washed with saturated aqueous sodium hydrogen carbonate and brine, then dried ($MgSO_4$) and concentrated under reduced pressure. Crystallisation of the residue from dichloromethane-hexane gave the *title compound* **15** (1.85 g, 59%) as white needles, mp 104 - 106 °C (Found: M^+, 334.0681. $C_{17}H_{18}S_2O_3$ requires *M*, 334.0693); υ_{max} 1704, 1596, 1574, 1320, 1304, 1261, 1149,

1085 and 1050 cm^{-1}; δ_H 2.42 and 2.48 (each 3 H, s, ArCH_3), 3.48 and 3.94 (each 1 H, dd, *J* 13, 2, 3-H), 6.02 and 6.28 (each 1 H, m, 1-H) and 7.15 - 7.78 (8 H, m, ArH); *m/z* (EI) 334 (M^+, 70%).

3-(4-Methylphenylsulfonyl)-2-(4-methoxyphenylsulfinyl)propene **16**

A solution of *m*-chloroperbenzoic acid (1.95 g, 11.3 mmol) in dichloromethane (50 cm^3) was added dropwise to a solution of the sulfide **14** (3.15 g, 9.4 mmol) in dichloromethane (150 cm^3) under argon at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and allowed to warm to -60 °C over 0.5 h, before being poured onto a mixture of ether (500 cm^3) and water (500 cm^3). The organic layer was washed with saturated aqueous sodium sulfite, saturated aqueous sodium hydrogen carbonate and brine, then dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the residue using ethyl acetate-light petroleum (1:1) as eluent gave the *title compound* **16** (2.28 g, 69%) as a white solid, mp 115 - 117 °C (Found: M^+, 350.0650. $C_{17}H_{18}S_2O_4$ requires *M*, 350.0646); υ_{max} 1594, 1496, 1321, 1256, 1150, 1086 and 1052 cm^{-1}; δ_H 2.38 (3 H, s, ArCH_3), 3.40 (1 H, d, *J* 15, 3-H), 3.77 (3 H, s, OCH_3), 3.83 (1 H, d, *J* 15, 3-H'), 5.94 and 6.21 (each 1 H, m, 1-H) and 6.21, 6.86, 7.25 and 7.63 (each 2 H, d, *J* 8, ArH); *m/z* (EI) 350 (M^+, 2%), 238 (6) and 155 (100).

[2-(4-Methylphenylsulfinyl)prop-2-enyl](tributyl)stannane **17**

Tributyltin hydride (4.0 g, 13.8 mmol) was added to a degassed solution of the sulfone **15** (2.0 g, 6.0 mmol) in benzene (50 cm^3) containing a trace of AIBN under an atmosphere of argon. The reaction mixture was heated under reflux for 7 h and then concentrated under reduced pressue. Flash chromatography of the residue using ether-light petroleum (1:8) as eluent gave the *title compound* **17** (2.29 g, 82%) as a colourless oil; δ_H 0.80 - 1.75 (29 H, m, CH_2SnBu_3), 2.40 (3 H, s, ArCH_3), 5.31 and 5.78 (each 1 H, m, 1-H) and 7.54 and 7.78 (each 2 H, d, *J* 8, ArH); *m/z* (CI) 471 ($M^+ + 1$, 9%), 431 (5), 413 (93) and 308 (100).

2-(4-Methoxyphenylsulfinyl)prop-2-en-1yl](tributyl)stannane **18**

Tributyltin hydride (3.6 g, 12.4 mmol) was added to a degassed solution of the sulfone **16** (1.84 g, 5.26 mmol) in benzene (40 cm^3) containing a trace of AIBN under an atmosphere of argon. The reaction mixture was heated under reflux for 6 h and then concentrated under reduced pressure. Flash chromatography of the residue using ether-light petroleum (1:4) as eluent gave the *title compound* **18** (1.54 g, 58%) as a colourless oil; υ_{max} 1594, 1495, 1463, 1304, 1253, 1084 and 1045 cm^{-1}; δ_H 0.80 - 1.50 (27 H, m, $SnBu_3$), 1.72 (2 H, m, 1-H_2), 3.84 (3 H, s, OCH_3), 5.30 and 5.79 (each 1 H, s, 3-H), and 6.98 and 7.56 (each 2 H, d, *J* 8, ArH); *m/z* (EI) 487 (M^+ + 1, 0.4%), 446 (32) and 429 (60).

1-(4-Nitrophenyl)-3-(4-methylphenylsulfinyl)but-3-en-1-ols **19** *and* **20**

Titanium tetrachloride (1.0 M in dichloromethane, 1.3 cm^3, 1.3 mmol) was added dropwise to a solution of 4-nitrobenzaldehyde (50 mg, 0.33 mmol) in dichloromethane (3 cm^3) under argon at -78 °C. A solution of the stannane **17** (200 mg, 0.43 mmol) in dichloromethane (1 cm^3) was added and the reaction mixture stirred at -78 °C for 2 h, allowed to warm to room temperature, and stirred for a further 2 h. Water (2 cm^3) was added and the reaction mixture diluted with dichloromethane (25 cm^3), washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography of the residue using ethyl acetate-light petroleum (1:1) as eluent gave the *title compounds* **19** and **20** (57 mg, 52%) as an oil, ratio = 80 : 20 (^1H NMR), mp 111-113 °C (Found: C, 61.5; H, 5.2; N, 4.1; S, 10.1. $C_{17}H_{17}NO_4S$ requires C, 61.6; H, 5.2; N, 4.2; S, 9.7%); υ_{max} 3356, 1600,

1521, 1346, 1109, 1081, 1013, 854 and 812 cm^{-1}; δ_H (major isomer) 2.42 (3 H, s, ArCH_3), 2.57 (1 H, dd, *J* 15, 7, 2-H), 2.67 (1 H, dd, *J* 15, 5, 2-H'), 5.04 (1 H, m, 1-H), 5.12 (1 H, s, 4-H), 5.28 (1 H, d, *J* 7, OH), 5.88 (1 H, s, 4-H'), 7.2 - 7.5 (6 H, m, ArH) and 8.1 (2 H, d, *J* 8, ArH); *m/z* (CI) 332 (M^+ + 1, 27%).

A solution of 4-nitrobenzaldehyde (100 mg, 0.66 mmol) and stannane **17** (400 mg, 0.85 mmol) in toluene (2 cm^3) was heated under reflux under argon for 18 h. After cooling and concentration under reduced pressure, flash chromatography of the residue using ethyl acetate-light petroleum (1:1) as eluent gave the title compounds **19 and 20** (120 mg, 55%) as a pale yellow oil, ratio = 55:45 (^{1}H NMR); δ_H (second isomer) 2.32 (1 H, dd, *J* 15, 10, 2-H), 2.42 (3 H, s, ArCH_3), 2.5 (1 H, dd, *J* 15, 5, 2-H'), 4.74 (1 H, dt, *J* 8, 2, 1-H), 5.31 (1 H, bs, OH), 5.86 and 6.14 (each 1 H, s, 4-H) and 7.28 - 8.15 (8 H, m, ArH).

1-(4-Nitrophenyl)-3-(4-methoxyphenylsulfinyl)but-3-en-1-ols **21** *and* **22**

Titanium tetrachloride (1.0 M in dichloromethane, 1.0 cm^3, 1.0 mmol) was added dropwise to a solution of 4-nitrobenzaldehyde (48 mg, 0.32 mmol) in dichloromethane (2 cm^3) under argon at -78 °C. A solution of the stannane **18** (250 mg, 0.51 mmol) in dichloromethane (1 cm^3) was added and the reaction mixture stirred at -78 °C for 2 h, allowed to warm to room temperature, and stirred for a further 18 h. Water (2 cm^3) was added, and the mixtue diluted with dichloromethane (25 cm^3), washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the residue using ethyl acetate petroleum (2:1) as eluent gave the *title compounds* **21** and **22** (60 mg, 55%) as an oil, ratio = 89.11 (Found: M^+ + H, 348.0893. $C_{17}H_{18}NO_5S$ requires *M*, 348.0827); υ_{max} 3345, 1594, 1519, 1496, 1347, 1307, 1256, 1125, 1109, 1085, 1027, 932, 855 and 832 cm^{-1}; δ_H (major isomer) 2.6 (1 H, dd, *J* 15, 5, 2-H), 2.7 (1 H, dd, *J* 15, 4, 2-H'), 3.87 (3 H, s, OCH_3),5.03 (1 H, m, 1-H), 5.13 (1 H, s, 4-H), 5.32 (1 H, d, *J* 8, OH) 5.89 (1 H, s, 4-H') and 7.03, 7.45, 7.51 and 8.15 (each 2 H, d, *J* 8, ArH); *m/z* (CI) 348 (M^+ + 1, 71%) and 197 (100).

A solution of 4-nitrobenzaldehyde (50 mg, 0.33 mmol) and stannane **18** (240 mg, 0.49 mmol) in toluene (2 cm^3) was heated under reflux under argon for 4 h. After cooling and concentration under reduced pressure, flash chromatography of the residue using ethyl acetate-light petroleum (2:1) as eluent gave the title compounds **21** and **22** (45 mg, 40%) as an oil, ratio = 54:46 (^{1}H NMR); δ_H (second isomer) 2.35 (1 H, dd, *J* 15, 10, 2-H), 2.5 (1 H, m, 2-H'), 3.85 (3 H, s, OCH_3), 4.27 (1 H, m, 1-H), 5.3 (1 H, bs, OH), 5.83 and 6.15 (each 1 H, s, 4-H) and 6.95 - 8.18 (8 H, m, ArH).

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