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Alkene Synthesis from Allylic Sulfones: Preparation of Isopropenyl and Isopropylidene Isomers from a Common Intermediate

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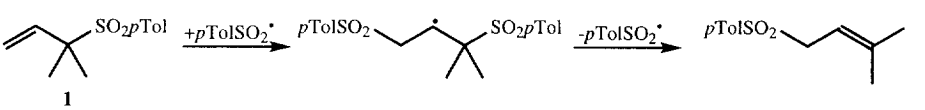
Abstract: Using α-alkylation, 1,3-rearrangement, and regioselective desulfonylation allows the control of the regiochemistry of alkene synthesis from allylic sulfones. Sequences involving allylic 2-hydroxypropyl, 2-trimethylsilylethyl, and benzothiazol-2-yl sulfones are described leading to isopropenyl and isopropylidene isomers of an alkene starting from a common sulfone intermediate. Copyright © 1996 Elsevier Science Ltd

Reports from both our own[1] and other[2] laboratories have documented that, under suitable conditions, allylic sulfones can undergo a 1,3-rearrangement reaction. Following our initial observations that allylic sulfones such as **1** underwent 1,3-rearrangement under free radical conditions initiated by benzoyl peroxide (BPO) or *p*–toluenesulfinic acid (Scheme 1), we proceeded to investigate more complex rearrangement and intermolecular addition sequences involving sulfonyl radicals.[3] Our interest in the 1,3-rearrangement reaction of sulfones was motivated, in part, by the potential synthetic utility of the reaction, in which the activating sulfonyl group is transferred from one end to the other of the allylic system. When allylic sulfones are intended as precursors of alkenes, reductive desulfonylation is frequently non-regioselective, presumably due to non-regioselective proton transfer to an intermediate ambident allylic anion.[4] However, Baldwin and co-workers[5] have reported the regioselective desulfonylation of allylic β-ketosulfones, considered to occur *via* the regioselective, retro-ene-type, loss of SO_2 from an intermediate allylic sulfinic acid (Scheme 2).



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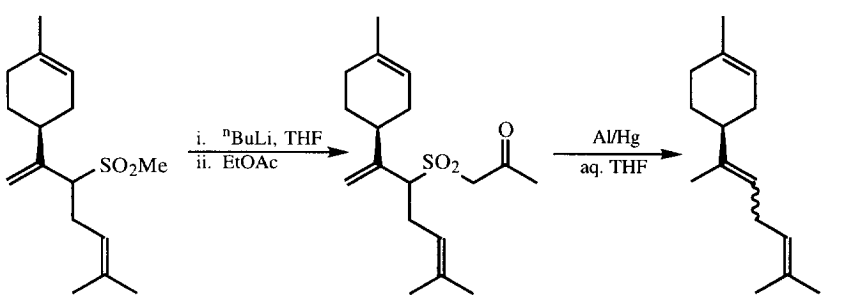
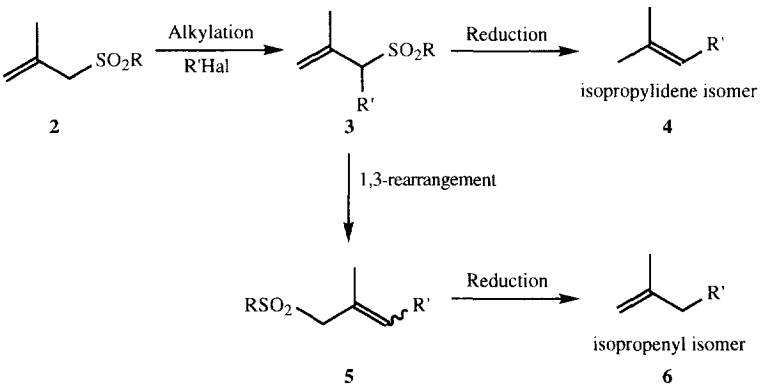
Scheme 1



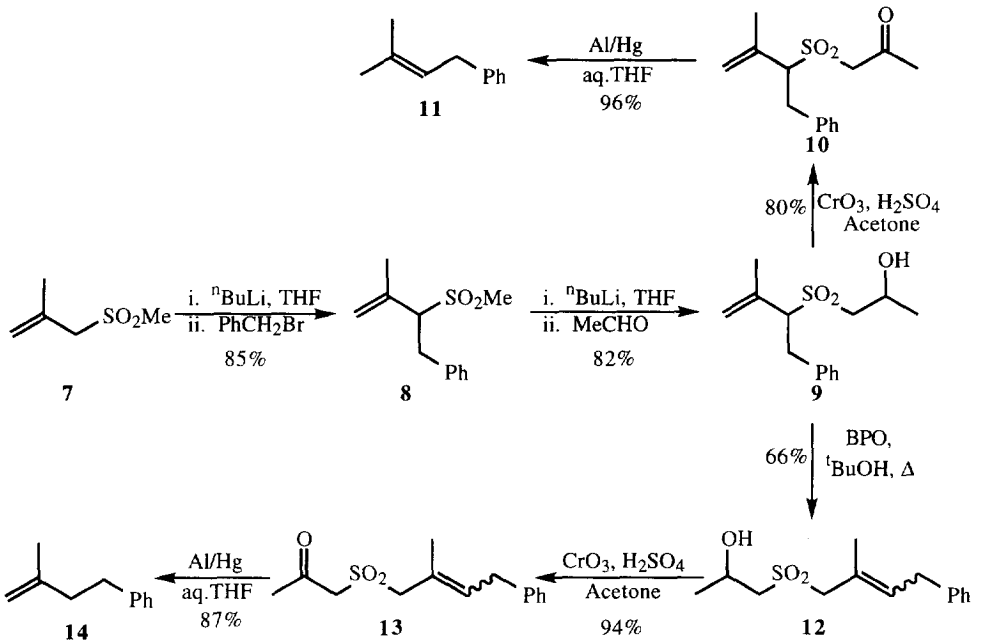
Scheme 2

We considered that the availability of a method for the 1,3-rearrangement which could be used in conjunction with regioselective desulfonylation could be synthetically useful, allowing either of the regioisomers which would be obtained from a non-regioselective allylic sulfone reduction to be obtained selectively. Thus, as an illustrative case, we sought to use a methallyl sulfone **2** as a precursor of either the isopropylidene **4** or isopropenyl **6** isomers of an alkene (Scheme 3), a classic problem of terpene chemistry. In essence, the idea was to alkylate the methallyl sulfone **2** to give the substituted sulfone **3**, followed either by desulfonylation directly to give **4**, or 1,3-rearrangement to give **5** and then desulfonylation, leading to the isomer **6**.



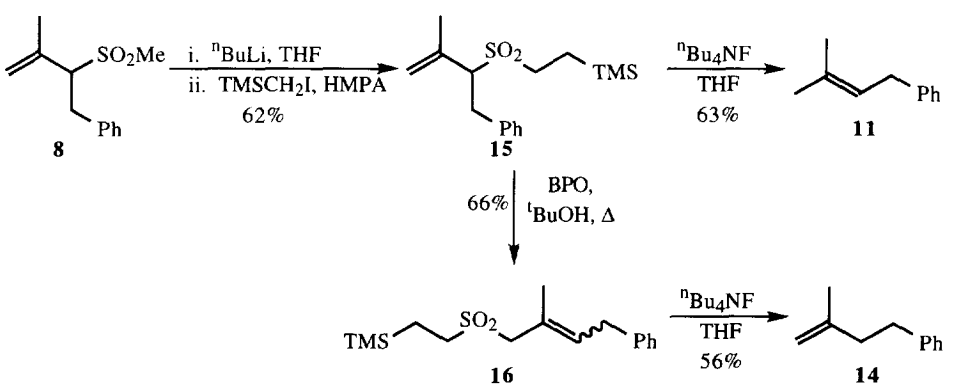
Scheme 3

Our initial approach is summarised in Scheme 4. Methallyl methyl sulfone **7** was metallated (^{n}BuLi, THF) then alkylated ($PhCH_2Br$) to give the substituted sulfone **8**. Metallation of **8** followed by hydroxyalkylation with acetaldehyde resulted in substitution at the methyl group (now the more readily deprotonated site) with formation of the β-hydroxysulfone **9** (as a 1:1 mixture of diastereoisomers). Oxidation of **9** using Jones reagent afforded the β-ketosulfone **10**, which, on reduction with aluminium amalgam led to 2-methyl-4-phenyl-2-butene **11** with the isopropylidene structure. In a complementary sequence, the β-hydroxysulfone **9** underwent 1,3-rearrangement under radical conditions (BPO, ^{t}BuOH, Δ) to give the β-hydroxysulfone **12** (*E*/*Z*~3:1). Subsequent oxidation to give **13** then reduction as before led to 2-methyl-4-phenyl-1-butene **14** the isopropenyl isomer of **11**. Although it was possible to acylate **8** (^{n}BuLi, EtOAc) to give the β-ketosulfone **11** directly, it was necessary to perform the 1,3-rearrangement at the hydroxysulfone oxidation level. This stems from the fact that allylic β-ketosulfones are not suitable substrates for the free radical rearrangement, apparently due to the ready loss of sulfur dioxide from the intermediate β-ketosulfonyl radical.[6]



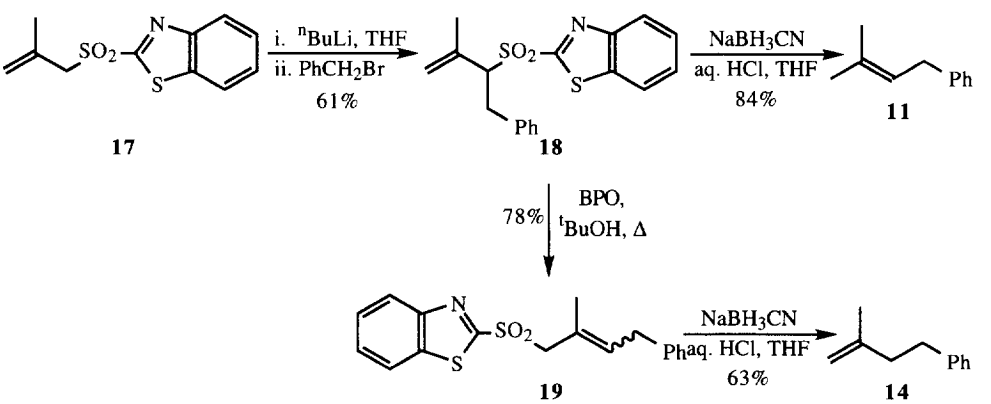
Scheme 4

We therefore sought an alternative sulfone substituent which would allow both the 1,3-rearrangement and desulfonylation to be carried out directly. We considered first the possibility of using allylic β-(trimethylsilyl)ethyl allylic sulfones as precursors to allylic sulfinic acids. Fluoride-induced elimination of the silyl and sulfonyl groups from β-trimethylsilyl sulfones has been used as the basis of alkene synthesis,[7] and the β-trimethylsilylethyl group is well known as a protecting group for carboxylic acids.[8] Thus, in an alternative sequence (Scheme 5) starting from the methyl sulfone **8**, metallation (^nBuLi, THF) followed by alkylation with $TMSCH_2I$ in the presence of HMPA gave the β-(trimethylsilyl)ethyl sulfone **15** which underwent desulfonylation with $^nBu_4NF$ to give, selectively, alkene **11**. Alternatively 1,3-rearrangement (BPO, ^tBuOH, Δ) of sulfone **15** with BPO in ^tBuOH gave **16** which underwent fluoride-induced desulfonylation to give alkene **14**.



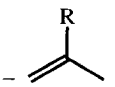
Scheme 5

Recent work on benzothiazol-2-yl sulfones by S.Julia and co-workers[9] suggested that allylic benzothiazolyl sulfones might also serve as precursors of allylic sulfinic acids. Easily prepared (by alkylation followed by oxidation) from readily available 2-mercaptobenzothiazole, these could be particularly useful in the present context, with no further modification of the sulfone group necessary prior to desulfonylation. Benzothiazol-2-yl methallyl sulfone **17** was prepared in this way by allylation using methallyl chloride followed by oxidation with hydrogen peroxide in the presence of ammonium molybdate.[10] Treatment of sulfone **17** with lithium diisopropylamide (LDA) followed by hydrogen peroxide then gave the monobenzylated sulfone **18**. Treatment of **18** with BPO in ^{t}BuOH gave the rearranged sulfone **19** as a mixture (*E*/*Z* ~7:2) of isomers. We envisaged that nucleophilic *ipso* substitution at the 2-position of sulfones should lead to allylic sulfinic acids which would lose SO_2 giving alkenes **11** or **14** as before. Indeed, in preliminary experiments, we found that sulfones **18** and *E*-**19** could both be desulfonylated using KOH, EtOH, Δ; $NaBH_4$, EtOH, rt, or $NaBH_3CN$, aq.HCl (pH3), THF, rt; ethoxybenzothiazole was the *ipso* substitution product with ethanolic KOH, while benzothiazole was formed in the cases involving the complex hydrides. However, the desulfonylation of sulfone **18** with ethanolic KOH or $NaBH_4$ was non-selective, giving **14** as up to 15% of the alkene product, while **11** was formed as the only alkene product with $NaBH_3CN$. Desulfonylation of *E*-**19** was selective (giving **14** only) under the three sets of conditions. It is possible that, under certain reaction conditions, the allylic sulfinic acid and sulfinate anion are in equilibrium, and that the lack of regioselectitity is associated with formation of an intermediate allylic anion, loss of sulfur dioxide being more rapid from the more sterically congested allylic sulfinate anion derived from sulfone **18**. In preparative experiments, treatment of sulfone **18** with $NaBH_3CN$ selectively gave alkene **11** in 84% yield, while treatment of sulfone **19** under the same conditions gave **14** in 63% yield (Scheme 6).



Scheme 6

Thus, three methods were found by which our original objective of using α-alkylation, 1,3-rearrangement, and regioselective desulfonylation to control the regiochemistry of alkene synthesis from allylic sulfones could be achieved. The benzothiazol-2-yl sulfones in particular appear to be potentially versatile substrates, given the ready availability of the thiol and simplicity of the transformations. In a retrosynthetic context, our approach allows an allylic sulfone to serve as an equivalent of either propen-1-yl or propen-3-yl anions, **20** or **21**.[11]



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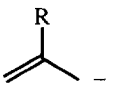

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EXPERIMENTAL

^{1}H n.m.r. spectra were recorded using Varian Gemini-200 (200MHz), Brucker WH300 (300MHz), or Brucker AM500 (500MHz) spectrometers; ^{13}C n.m.r. spectra were recorded using Varian Gemini-200 (50.3MHz), Brucker AM250 (62.9MHz), or Brucker AM500 (125.8MHz) spectrometers. Chemical shifts are quoted in p.p.m. downfield from TMS. Infra-red spectra were recorded using a Perkin Elmer 1710 Fourier transform i.r. spectrophotometer. Mass spectra were recorded using V.G. Mass lab Trio-1, Micromass ZAB 1F, or V.G. Mass lab 20-250 instruments, using chemical ionisation (CI), desorption chemical ionisation (DCI), electron impact (EI), or fast atom bombardment (FAB) as the ionisation technique. Only selected peaks from infra-red and mass spectra are quoted. Solvents and reagents described as 'dry' were purified by standard methods.[12] Benzoyl peroxide (BPO) was recrystallised from $CHCl_3$ / MeOH. "Light petroleum" refers to the fraction boiling at 30-40°C unless indicated. ^{n}BuLi was used as a solution of approximately 1.6M concentration in hexanes, and standardised by titration against 1,3-diphenyl-2-propanone *p*-toluenesulfonylhydrazone.[13]

3-Methanesulfonyl-2-methyl-1-propene (7). 3-Chloro-2-methyl-1-propene (60ml, 55g, 0.61mol), sodium methanesulfinate[14] (42.84g, 0.40mol), tetra-*n*-butylammonium bromide (9.68g, 30mmol), acetone (100ml), toluene (100ml), and water (135ml) were vigorously stirred at 75°C (bath temperature) for 21h then allowed to cool. The solution was partitioned between water (200ml) and dichloromethane (200ml), the phases were separated, and the aqueous phase was extracted with further dichloromethane (2x200ml). The combined organic solution was dried ($MgSO_4$), filtered, and evaporated. Distillation of the residue (55.7g) gave 4,4-bis(chloromethyl)-2-methyl-1-pentene (0.98g) as a colourless oil; b.p. 80-83°C at 0.8mbar (lit.[15] 75.5°C at 10mmHg); and 3-methanesulfonyl-2-methyl-1-propene **(7)** (40.62g, 0.303mol, 76%) as a crystalline solid; b.p. 106-107°C at 0.8mbar; m.p. 41-45°C (from ethanol) (lit.[16] 39-40°C); (Found: C, 44.7; H, 7.8. Calc. for $C_5H_{10}O_2S$: C, 44.75; H, 7.5%.); δ_H (300MHz; $CDCl_3$) 2.01 (3H, t, J=1Hz, =CC$\underline{H}_3$), 2.91 (3H, s, C$\underline{H}_3SO_2$), 3.71 (2H, s, C$\underline{H}_2SO_2$), 5.12 (1H, s, =C$\underline{H}$), 5.25 (1H, t, J=1Hz, =C$\underline{H}$); δ_C (50.3MHz; $CDCl_3$) 22.3 (q, =C$\underline{C}H_3$), 39.0 (q, $\underline{C}H_3SO_2$), 62.8 (t, $\underline{C}H_2SO_2$), 120.5 (t, C=$\underline{C}H_2$), 134.5 (s, $\underline{C}$=CH_2); ν_{max} ($CHCl_3$) 1646, 1411, 1315, 1121, 963cm^{-1}; *m/z* (CI, NH_3) 152 (100%, MNH_4^+).

3-Methanesulfonyl-2-methyl-4-phenyl-1-butene (8). ^{n}BuLi (37.9mmol) was added to a solution of 3-methanesulfonyl-2-methyl-1-propene **(7)** (5.08g, 37.9mmol) stirred at -78°C (bath temperature) in dry THF (100ml) under argon. After 15min, benzyl bromide (5.4ml, 7.77g, 45.4mmol) was added. The mixture was stirred at -78°C for 1h, then the cooling bath was removed and stirring was continued for a further 1h at 16°C. Acetic acid (10ml) and water (100ml) were added, then the solution was extracted with dichloromethane (4x100ml). The combined organic extracts were washed with saturated aqueous sodium bicarbonate (2x200ml) and water (100ml), then dried ($MgSO_4$), filtered, and evaporated. The residue (9.62g) was recrystallised from ether / light petroleum to give 3-methanesulfonyl-2-methyl-4-phenyl-1-butene **8** (7.21g, 32.1mmol, 85%); m.p. 53-57°C; (Found: C, 64.35; H, 7.55. $C_{12}H_{16}O_2S$ requires: C, 64.25; H, 7.2%.); δ_H (300MHz; $CDCl_3$) 1.88

(3H, d, J=1Hz, =CC$\underline{H}_3$), 2.88 (3H, s, C$\underline{H}_3SO_2$), 3.09 (1H, dd, J=14, 11Hz, PhC$\underline{H}$), 3.54 (1H, dd, J=14, 4Hz, PhC$\underline{H}$), 3.84 (1H, dd, J=11, 4Hz, C$\underline{H}SO_2$), 5.09 (1H, s, C=C$\underline{H}$), 5.18 (1H, t, J=1Hz, C=C$\underline{H}$), 7.19-7.33 (5H, m, Ph); δ_C (50.3MHz; $CDCl_3$) 19.9 (q, =CCH_3), 30.8 (t, Ph$\underline{C}H_2$), 38.5 ($\underline{C}H_3SO_2$), 72.4 (d, $\underline{C}HSO_2$), 120.8 (t, C=$\underline{C}H_2$), 126.9 (d, Ph), 128.7 (d, Ph), 129.0 (d, Ph), 136.7 (s, =$\underline{C}CH_3$ or Ph), 137.4 (s, =$\underline{C}CH_3$ or Ph); ν_{max} ($CHCl_3$) 1642, 1604, 1497, 1307, 1136cm^{-1}; *m/z* (CI, NH_3) 242 (100%, MNH_4^+), 145 (60%, MH^+-$MeSO_2H$). The compound was found to be unstable and underwent spontaneous 1,3-rearrangement to give 1-methanesulfonyl-2-methyl-4-phenyl-2-butene over a few days when stored in the laboratory. It was, however, stable when stored over several months in a freezer at -20°C.

3-(2'-Hydroxy-1'-propanesulfonyl)-2-methyl-4-phenyl-1-butene (9). ^{n}BuLi (4.58mmol) was added to a solution of 3-methanesulfonyl-2-methyl-4-phenyl-1-butene **(8)** (1.00g, 4.46mmol) stirred at -78°C (bath temperature) in dry THF (50ml) under argon. After 5min, acetaldehyde (16% w/v in THF, 1.85ml, 6.71mmol) was added. The mixture was stirred at -78°C for 1h, then the cooling bath was removed and the stirring was continued for a further 2h at 20°C. Acetic acid (5ml) and water (100ml) were added and the solution was extracted with dichloromethane (2x100ml). The combined organic extracts were washed with saturated aqueous sodium bicarbonate (100ml), aqueous sodium metabisulfite (1M, 100ml), and water (100ml), then dried ($MgSO_4$), filtered, and evaporated. The residue (1.13g) was subjected to flash chromatography using ether / light petroleum (1:1 v/v) as the eluant to give recovered 3-methanesulfonyl-2-methyl-4-phenyl-1-butene **(8)** (126mg, 0.56mmol, 13%); and 3-(2'-hydroxy-1'-propanesulfonyl)-2-methyl-4-phenyl-1-butene **(9)** (983mg, 3.66mmol, 82%). The diastereoisomers of the product hydroxysulfone were present in a ratio of approximately 1:1 as estimated from the ^{1}H n.m.r. spectrum of the crude product, and were partially resolved during chromatography so that samples of each isomer were obtained: Isomer 1: m.p. 82.5-83.5°C (needles from ether / light petroleum); (Found: C, 62.95; H, 7.5. $C_{14}H_{20}O_3S$ requires: C, 62.65; H, 7.5%.); δ_H (500MHz; $CDCl_3$) 1.29 (3H, d, J=6Hz, C$\underline{H}_3$CHOH), 1.87 (3H, s, =CC$\underline{H}_3$), 2.98 (1H, dd, J=14, 2Hz, CH(OH)C$\underline{H}SO_2$), 3.06 (1H, d, J=3Hz, CHO$\underline{H}$), 3.09 (1H, dd, J=14, 11Hz, PhC$\underline{H}$), 3.19 (1H, dd, J=14, 10Hz, CH(OH)C$\underline{H}SO_2$), 3.55 (1H, dd, J=14, 4Hz, PhC$\underline{H}$), 3.96 (1H, dd, J=11, 4Hz, =CC$\underline{H}SO_2$), 4.52 (1H, m, C$\underline{H}$OH), 5.13 (1H, s, C=C$\underline{H}$), 5.20 (1H, t, J=1Hz, C=C$\underline{H}$), 7.18-7.48 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) 20.2 (q, $\underline{C}H_3$CHOH or =C$\underline{C}H_3$), 22.8 (q, $\underline{C}H_3$CHOH or =C$\underline{C}H_3$), 31.1 (t, Ph$\underline{C}H_2$), 57.9 (t, CH(OH)$\underline{C}H_2SO_2$), 62.6 (d, $\underline{C}$HOH), 72.6 (d, =$\underline{C}CHSO_2$), 121.3 (t, C=$\underline{C}H_2$), 127.0 (d, Ph), 128.7 (d, Ph), 128.9 (d, Ph), 136.7 (s, Ph or CH=$\underline{C}CH_3$), 137.3 (s, Ph or CH=$\underline{C}CH_3$); ν_{max} ($CHCl_3$) 3543, 1641, 1605, 1497, 1304, 1139cm^{-1}; *m/z* (CI, NH_3) 286 (75%, MNH_4^+), 145 (100%, MH^+-MeCH(OH)CH_2SO_2H). Isomer 2: m.p. 89-91.5°C (fine needles from ether / light petroleum); (Found: C, 62.85; H, 7.3. $C_{14}H_{20}O_3S$ requires: C, 62.65; H, 7.5%.); δ_H (500MHz; $CDCl_3$) 1.30 (3H, d, J=6Hz, C$\underline{H}_3$CHOH), 1.87 (3H, d, J=1Hz, =CC$\underline{H}_3$), 3.05-3.14 (3H, complex, CH(OH)C$\underline{H}_2SO_2$ and PhC$\underline{H}$), 3.25 (1H, d, J=3Hz, CHO$\underline{H}$), 3.52 (1H, dd, J=14, 4Hz, PhC$\underline{H}$), 3.94 (1H, dd, J=11, 4Hz, =CC$\underline{H}SO_2$), 4.50 (1H, m, C$\underline{H}$OH), 5.06 (1H, s, C=C$\underline{H}$), 5.19 (1H, t, J=1Hz, C=C$\underline{H}$), 7.18-7.48 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) 20.3 (q, $\underline{C}H_3$CHOH or =C$\underline{C}H_3$), 22.7 (q, $\underline{C}H_3$CHOH or =C$\underline{C}H_3$), 31.5 (t, Ph$\underline{C}H_2$), 57.7 (t, CH(OH)$\underline{C}H_2SO_2$), 62.4 (d, $\underline{C}$HOH), 72.1 (d, =$\underline{C}CHSO_2$), 121.0 (t, C=$\underline{C}H_2$), 127.0 (d, Ph), 128.7 (d, Ph), 129.0 (d, Ph), 136.7 (s, Ph or CH=$\underline{C}CH_3$), 137.3 (s, Ph or CH=$\underline{C}CH_3$); ν_{max} ($CHCl_3$) 3543, 1641, 1605, 1497, 1304, 1140cm^{-1}; 286 (76%, MNH_4^+), 145 (100%, MH^+-MeCH(OH)CH_2SO_2H).

1-(2'-Hydroxy-1'-propanesulfonyl)-2-methyl-4-phenyl-2-butene (12). A solution containing 3-(2'-hydroxy-1'-propanesulfonyl)-2-methyl-4-phenyl-1-butene (**9**) (3.00g, 11.18mmol) and BPO (540mg, 2.23mmol) in ^{t}BuOH (11ml) was heated at reflux temperature under argon for 72h. The solvent was evaporated under reduced pressure and the residue was subjected to flash chromatography using ether / light petroleum (1:1 v/v) as the eluant to give 1-(2'-hydroxy-1'-propanesulfonyl)-2-methyl-4-phenyl-2-butene (**12**) (1.99g, 7.42mmol, 66%) as a colourless solid (*E/Z* ratio estimated as approximately 3:1 by ^{1}H n.m.r.); (Found: C, 62.7; H, 7.45. $C_{14}H_{20}O_3S$ requires: C, 62.65; H, 7.5%.); δ_H (500MHz; $CDCl_3$) 1.23 (3H, d, J=6Hz, C$\underline{H}_3$CHOH, *E* isomer), 1.29 (3H, d, J=6Hz, C$\underline{H}_3$CHOH, *Z* isomer), 2.01 (3H, d, J=1Hz, =CC$\underline{H}_3$, *E* isomer), 2.03 (3H, d, 1Hz, =CC$\underline{H}_3$, *Z* isomer), 2.96-3.14 (3H, complex, CH(O$\underline{H}$)C$\underline{H}_2$SO$_2$), 3.48 (2H, m, PhC$\underline{H}_2$), 3.75 (1H, d, J=14Hz, =CC$\underline{H}$SO$_2$, *E* isomer), 3.79 (1H, d, J=14Hz, =CC$\underline{H}$SO$_2$, *E* isomer), 3.92 (1H, d, J=14Hz, =CC$\underline{H}$SO$_2$, *Z* isomer), 3.95 (1H, d, J=14Hz, =CC$\underline{H}$SO$_2$, *Z* isomer), 4.43 (1H, m, C$\underline{H}$OH, *E* isomer), 4.51 (1H, m, C$\underline{H}$OH, *Z* isomer), 5.75 (1H, tm, J=8Hz, C$\underline{H}$=CCH$_3$, *E* isomer), 5.90 (1H, m, C$\underline{H}$=CCH$_3$, *Z* isomer), 7.18-7.35 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) 16.8 (q, =C$\underline{C}$H$_3$, *Z* isomer), 22.7 (q, $\underline{C}$H$_3$CHOH, *E* isomer), 22.9 (q, $\underline{C}$H$_3$CHOH, *Z* isomer), 24.3 (q, =C$\underline{C}$H$_3$, *Z* isomer), 34.5 (t, Ph$\underline{C}$H$_2$, *E* isomer), 34.6 (t, Ph$\underline{C}$H$_2$, *Z* isomer), 57.5 (t, CH(OH)$\underline{C}$H$_2$SO$_2$, *Z* isomer), 58.5 (t, CH(OH)$\underline{C}$H$_2$SO$_2$, *E* isomer), 60.4 (t, =C$\underline{C}$H$_2$SO$_2$, *Z* isomer), 62.4 (d, $\underline{C}$HOH, *E* isomer), 62.5 (d, $\underline{C}$HOH, *Z* isomer), 64.3 (t, =C$\underline{C}$H$_2$SO$_2$), 123.4 (s, CH=$\underline{C}$CH$_3$, *Z* isomer), 124.5 (s, CH=$\underline{C}$CH$_3$, *E* isomer), 126.1 (d, Ph), 128.1 (d, Ph), 128.2 (d, Ph), 128.5 (d, Ph), 133.5 (d, $\underline{C}$H=CCH$_3$, *Z* isomer), 134.6 (d, $\underline{C}$H=CCH$_3$, *E* isomer), 139.6 (s, Ph); ν_{max} ($CHCl_3$) 3543, 1603, 1495, 1309, 1125cm^{-1}; *m/z* (DCI, NH_3) 286 (17%, MNH_4^+), 145 (100%, MH^+-$CH_3CH(OH)CH_2SO_2H$).

Procedure for oxidation of hydroxysulfones using chromium trioxide / aqueous sulfuric acid. Chromium trioxide (20.0g, 0.20mol) was dissolved in water (40ml). Concentrated sulfuric acid (32.0g, 0.32mol) was cautiously added, then the resulting solution was diluted to 100ml total volume with water. A portion of the resulting solution (*ca.* 2eq. Cr^{VI}) was added to a solution of the hydroxysulfone (1eq.) dissolved in acetone. The resulting solution was stirred for 2-3h at room temperature. The solution was diluted with water, extracted with three portions of dichloromethane, then the combined organic extracts were washed three portions of water, dried ($MgSO_4$), filtered, and evaporated. The crude ketosulfone was purified either by recrystallisation or by flash chromatography using an ether / light petroleum mixture as the eluant. The following ketosulfones were prepared by this method:

2-Methyl-3-(2'-oxo-1'-propanesulfonyl)-4-phenyl-1-butene (10). Prepared by the oxidation of 3-(2'-hydroxy-1'-propanesulfonyl)-2-methyl-4-phenyl-1-butene (**9**). The crude product was recrystallised from ether / light petroleum to give 2-methyl-3-(2'-oxo-1'-propanesulfonyl)-4-phenyl-1-butene (**10**) (80%) as a crystalline solid; m.p. 58-60°C (from ether / *n*-pentane); (Found: C, 63.2; H, 6.8. $C_{14}H_{18}O_2S$ requires: C, 63.15; H, 6.8%.); δ_H (300MHz; $CDCl_3$) 1.85 (3H, s, =CC$\underline{H}_3$), 2.41 (3H, s, C$\underline{H}_3$C=O), 3.08 (1H, dd, J=14, 11Hz, PhC$\underline{H}$), 3.51 (1H, dd, J=14, 4Hz, PhC$\underline{H}$), 3.93 (1H, d, J=14Hz, CH$_3$COC$\underline{H}$SO$_2$), 4.16 (1H, d, J=14Hz, CH$_3$COC$\underline{H}$SO$_2$), 4.19 (1H, dd, J=11, 4Hz, =CC$\underline{H}$SO$_2$), 5.20 (2H, broad s, C=C$\underline{H}_2$), 7.18-7.33 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) 20.2 (q, =C$\underline{C}$H$_3$), 31.2 (t, Ph$\underline{C}$H$_2$), 31.8 (q, $\underline{C}$H$_3$C=O), 61.3 (t, CH$_3$CO$\underline{C}$H$_2$SO$_2$), 71.0 (d, =C$\underline{C}$HSO$_2$), 121.6 (t, C=$\underline{C}$H$_2$), 126.9 (d, Ph), 128.6 (d, Ph), 128.9 (d, Ph), 136.4 (s, Ph or $\underline{C}$=CH$_2$), 136.9 (s, Ph or $\underline{C}$=CH$_2$), 197.0 (s, C=O); ν_{max} ($CHCl_3$) 1721, 1640, 1605, 1497, 1317, 1150cm^{-1}; δ_H (300MHz; $CDCl_3$) 1.85 (3H, s, =CC$\underline{H}_3$), 2.41 (3H, s, C$\underline{H}_3$C=O), 3.08 (1H, dd, J=13.9,

11.2Hz, PhC<u>H</u>), 3.51 (1H, dd, J=13.9, 3.9Hz, PhC<u>H</u>), 3.93 (1H, d, J=14.1Hz, $CH_3COC\underline{H}SO_2$), 4.16 (1H, d, J=14.1Hz, $CH_3COC\underline{H}SO_2$), 4.19 (1H, dd, J=11.2, 4.1Hz, $=CC\underline{H}SO_2$), 5.20 (2H, broad s, $C=C\underline{H}_2$), 7.18-7.33 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) 20.16 (q, $=C\underline{C}H_3$), 31.24 (t, $Ph\underline{C}H_2$), 31.82 (q, $\underline{C}H_3C=O$), 61.26 (t, $CH_3CO\underline{C}H_2SO_2$), 71.03 (d, $=C\underline{C}HSO_2$), 121.57 (t, $C=\underline{C}H_2$), 126.91 (d, Ph), 128.58 (d, Ph), 128.90 (d, Ph), 136.38 (s, Ph or $\underline{C}=CH_2$), 136.90 (s, Ph or $\underline{C}=CH_2$), 196.99 (s, C=O); *m/z* (CI, NH_3) 284 (100%, MNH_4^+), 145 (45%, MH^+-$CH_3COCH_2SO_2H$).

2-Methyl-1-(2'-oxo-1'-propanesulfonyl)-4-phenyl-2-butene (13). Prepared by the oxidation of 1-(2'-hydroxy-1'-propanesulfonyl)-2-methyl-4-phenyl-2-butene (**12**). The crude product was subjected to flash chromatography using ether / light petroleum (1:2 v/v) as the eluant to give 2-methyl-1-(2'-oxo-1'-propanesulfonyl)-4-phenyl-2-butene (**13**) (84%) as an oil; (Found: C, 63.7; H, 7.1. $C_{14}H_{18}O_3S$ requires: C, 63.15; H, 6.8%.); δ_H (500MHz; $CDCl_3$) 1.99 (3H, d, J=1Hz, $=CC\underline{H}_3$, *E* isomer), 2.01 (3H, d, J=1Hz, $=CC\underline{H}_3$, *Z* isomer), 2.34 (3H, s, $C\underline{H}_3CO$, *E* isomer), 2.41 (3H, s, $C\underline{H}_3CO$, *Z* isomer), 3.47 (2H, d, J=8Hz, $PhC\underline{H}_2$, *E* isomer), 3.49 (2H, d, J=8Hz, $PhC\underline{H}_2$, *Z* isomer), 3.83 (2H, s, $=CC\underline{H}_2SO_2$ or $COC\underline{H}_2SO_2$, *E* isomer), 3.98 (2H, s, $=CC\underline{H}_2SO_2$ or $COC\underline{H}_2SO_2$, *E* isomer), 4.03 (4H, s, $=CC\underline{H}_2SO_2$ and $COC\underline{H}_2SO_2$, *Z* isomer), 5.86 (1H, tm, J=8Hz, $C\underline{H}=CCH_3$, *E* isomer), 5.90 (1H, tm, J=8Hz, $C\underline{H}=CCH_3$, *Z* isomer), 7.17-7.32 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) 16.9 (q, $=C\underline{C}H_3$, *E* isomer), 24.4 (q, $=C\underline{C}H_3$, *Z* isomer), 31.8 (q, $\underline{C}H_3CO$, *E* isomer), 31.9 (q, $\underline{C}H_3CO$, *Z* isomer), 34.6 (t, $Ph\underline{C}H_2$), 56.8 (t, $=C\underline{C}H_2SO_2$, *Z* isomer), 61.7 (t, $=C\underline{C}H_2SO_2$, *E* isomer), 63.2 (t, $CO\underline{C}H_2SO_2$, *E* isomer), 64.0 (t, $CO\underline{C}H_2SO_2$, *Z* isomer), 122.7 (s, $CH=\underline{C}CH_3$, *Z* isomer), 124.4 (s, $CH=\underline{C}CH_3$, *E* isomer), 126.2 (d, Ph), 128.2 (d, Ph, *E* isomer), 128.3 (d, Ph, *Z* isomer), 128.5 (d, Ph, *Z* isomer), 128.6 (d, Ph, *E* isomer), 134.5 (d, $\underline{C}H=CCH_3$, *Z* isomer), 135.2 (d, $\underline{C}H=CCH_3$, *E* isomer), 139.6 (s, Ph, *E* isomer), 139.8 (s, Ph, *Z* isomer), 197.1 (s, $\underline{C}=O$); ν_{max} ($CHCl_3$) 1721, 1603, 1495, 1323, 1117cm^{-1}; *m/z* (CI, NH_3) 284 (47%, MNH_4^+), 145 (100%, MH^+-$CH_3COCH_2SO_2H$), 91 (47%, $C_7H_7^+$).

Procedure for the reduction of allylic 2-oxopropyl sulfones using aluminium amalgam. A solution of the ketosulfone in aqueous THF (90% v/v; *ca.* 25ml$mmol^{-1}$) was deoxygenated for 10min using a stream of argon. Excess aluminium amalgam[17] (*ca.* 20eq. Al, prepared from coarsely powdered aluminium) was added, then the solution was stirred under argon at room temperature for 24h. The solution was filtered through celite which was then washed with ether, then the combined filtrate was washed with water and brine, dried ($MgSO_4$), filtered, and evaporated. The alkene was then purified by flash chromatography using light petroleum as the eluant. The following alkenes were prepared by this method:

3-Methyl-1-phenyl-2-butene (11). Prepared by the reduction of 2-methyl-3-(2'-oxo-1'-propanesulfonyl)-4-phenyl-1-butene (**10**). The crude product was subjected to flash chromatography using light petroleum as the eluant to give 3-methyl-1-phenyl-2-butene (**11**) (96%) as an oil; b.p. 150°C at 12mmHg (kugelrohr) (lit.[18] 99-103°C at 25mmHg); δ_H (500MHz; $CDCl_3$) 1.75 (3H, s, $=CC\underline{H}_3$), 1.78 (3H, d, J=1Hz, $=CC\underline{H}_3$), 3.38 (2H, d, J=7Hz, $PhC\underline{H}_2$), 5.37 (1H, tm, J=7Hz, $C\underline{H}=C(CH_3)_2$), 7.18-7.32 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) 17.7 (q, $=C\underline{C}H_3$), 25.6 (q, $=C\underline{C}H_3$), 34.4 (t, $Ph\underline{C}H_2$), 123.4 (d, Ph or $\underline{C}H=C(CH_3)_2$), 125.7 (d, Ph or $\underline{C}H=C(CH_3)_2$), 128.3 (d, Ph), 132.3 (s, Ph), 141.9 (s, $CH=\underline{C}(CH_3)_2$); ν_{max} ($CHCl_3$) 1603, 1494, 1453, 1377, 1103, 1073, 1030, 855, 700cm^{-1}; *m/z* (CI, NH_3) 164 (1%, MNH_4^+), 147 (8%, MH^+), 146 (71%, M^+), 131 (100%), 91 (46%, $C_7H_7^+$).

2-Methyl-4-phenyl-1-butene (14). Prepared by the reduction of 2-methyl-1-(2'-oxo-1'-propanesulfonyl)-4-phenyl-2-butene **(13)**. The crude product was subjected to flash chromatography using light petroleum as the eluant to give 2-methyl-4-phenyl-1-butene **(14)** (87%) as an oil; b.p. 135-140°C at 35mmHg (kugelrohr) (lit.[18] 76-78°C at 12mmHg); δ_H (500MHz; $CDCl_3$) 1.79 (3H, s, =CC$\underline{H}_3$), 2.34 (2H, t, J=8Hz, =CC$\underline{H}_2$), 2.77 (2H, t, J=8Hz, PhC$\underline{H}_2$), 4.73 (1H, s, =C$\underline{H}$), 4.76 (1H, d, J=1Hz, =C$\underline{H}$), 7.17-7.32 (5H, m, Ph); δ_C (50.3MHz; $CDCl_3$) 22.4(q, =C$\underline{C}H_3$), 34.1 (t, =C$\underline{C}H_2$), 39.5 (t, Ph$\underline{C}H_2$), 110.3 (t, C=$\underline{C}H_2$), 125.9 (d, Ph), 128.4 (d, Ph), 142.4 (s, Ph or C=CH_2), 145.5 (s, Ph or $\underline{C}$=CH_2); ν_{max} ($CHCl_3$) 1649, 1604, 1495, 1454, 1376, 1079, 1031, 893, 700cm^{-1}; *m/z* (CI, NH_3) 164 (33%, MNH_4^+), 147 (4%, MH^+), 146 (32%, M^+), 108 (53%, $PhCH_2NH_3^+$), 91 (100%, $C_7H_7^+$).

2-Methyl-4-phenyl-3-(2'-trimethylsilyl-1'-ethanesulfonyl)-1-butene (15). ^{n}BuLi (4.46mmol) was added to a solution of 3-methanesulfonyl-2-methyl-4-phenyl-1-butene **(8)** (1.00g, 4.46mmol) stirred at -78°C (bath temperature) in dry THF (10ml) under argon. After 5min, iodomethyltrimethylsilane (3.31ml, 4.78g, 22.3mmol) and HMPA (1.55ml, 1.60g, 8.91mmol) were added. The mixture was stirred at -78°C for 1h, then the cooling bath was removed and stirring was continued for a further 2h at 21°C. Water (50ml) was added and the solution was extracted with dichloromethane (4x50ml). The combined organic extracts were washed with water (50ml), then dried ($MgSO_4$), filtered, and evaporated. The residue (4.04g) was subjected to flash chromatography using ether / light petroleum (1:9 v/v) as the eluant to give *E*-3-methyl-1-phenyl-5-trimethylsilyl-2-(2'-trimethylsilyl-1'-ethanesulfonyl)-2-pentene (122mg, 0.31mmol, 7%) as a crystalline solid; m.p. 92-95°C (needles from light petroleum); (Found: C, 60.6; H, 9.55%. $C_{20}H_{36}O_2SSi_2$ requires: C, 60.55; H, 9.15%.); δ_H (500MHz; $CDCl_3$) -0.52 (9H, s, ($C\underline{H}_3$)$_3$Si), -0.10 (9H, s, ($C\underline{H}_3$)$_3$Si), 0.64 (2H, m, $Me_3SiC\underline{H}_2CH_2C$=), 0.87 (2H, m, $Me_3SiC\underline{H}_2CH_2SO_2$), 2.25 (2H, m, $Me_3SiCH_2C\underline{H}_2C$), 2.28 (3H, s, =CC$\underline{H}_3$), 2.64 (2H, m, $Me_3SiCH_2C\underline{H}_2SO_2$), 3.88 (2H, s, PhC$\underline{H}_2$), 7.21-7.29 (5H, m, Ph); δ_C (50.3MHz; $CDCl_3$) -2.4 (q, ($\underline{C}H_3$)$_3$Si), -2.3 (q, ($\underline{C}H_3$)$_3$Si), 7.6 (t, $Me_3Si\underline{C}H_2CH_2C$=), 14.6 (t, $Me_3Si\underline{C}H_2CH_2SO_2$), 19.9 (q, =C$\underline{C}H_3$), 32.1 (t, $Me_3SiCH_2\underline{C}H_2C$=). 34.5 (t, Ph$\underline{C}H_2$), 51.8 (t, $Me_3SiCH_2\underline{C}H_2SO_2$), 126.5 (d, Ph), 128.4 (d, Ph), 128.6 (d, Ph), 132.9 (s, Ph or C(CH_3)=$\underline{C}SO_2$), 138.7 (s, Ph or C(CH_3)=$\underline{C}SO_2$), 156.1 (s, $\underline{C}(CH_3)$=CSO_2); ν_{max} ($CHCl_3$) 1495, 1454, 1304, 1253, 1165, 1126cm^{-1}; *m/z* (DCI, NH_3) 414 (13%, MNH_4^+), 91 (24%, $C_7H_7^+$), 90 (100%, $Me_3SiNH_3^+$), 73 (96%, Me_3Si^+); and 2-methyl-4-phenyl-3-(2'-trimethylsilyl-1'-ethanesulfonyl)-1-butene **(15)** (863mg, 2.78mmol, 62%) as a crystalline solid; m.p. 67-71°C [needles from light petroleum (b.p. 40-60°C)]; (Found: C, 62.2; H, 8.65%. $C_{16}H_{26}O_2SSi$ requires: C, 61.9; H, 8.45%.); δ_H (300MHz; $CDCl_3$) 0.04 (9H, s, ($C\underline{H}_3$)$_3$Si), 1.03 (2H, m, $Me_3SiC\underline{H}_2CH_2SO_2$), 1.89 (3H, s, =CC$\underline{H}_3$), 2.87 (2H, m, $Me_3SiCH_2C\underline{H}_2SO_2$), 3.10 (1H, dd, J=14, 11Hz, PhC$\underline{H}$), 3.52 (1H, dd, J=14, 4Hz, PhC$\underline{H}$), 3.90 (1H, dd, J=11, 4Hz, =CC$\underline{H}SO_2$), 5.05 (1H, s, C=C$\underline{H}$), 5.14 (1H, t, J=1Hz, C=C$\underline{H}$), 7.19-7.34 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) -2.1 (q, ($\underline{C}H_3$)$_3$Si), 8.5 (t, $Me_3Si\underline{C}H_2CH_2SO_2$), 20.1 (q, =C$\underline{C}H_3$), 31.6 (t, Ph$\underline{C}H_2$), 47.4 (t, $Me_3SiCH_2\underline{C}H_2SO_2$), 70.1 (d, =C$\underline{C}HSO_2$), 120.2 (t, C=$\underline{C}H_2$), 126.9 (d, Ph), 128.6 (d, Ph), 129.0 (d, Ph), 137.2 (s, Ph or $\underline{C}(CH_3)$=CH_2), 138.0 (s, Ph or $\underline{C}(CH_3)$=CH_2); ν_{max} ($CHCl_3$) 1641, 1605, 1497, 1455, 1309, 1254, 1130cm^{-1}; *m/z* (CI, NH_3) 328 (30%, MNH_4^+), 145 (94%, MH^+-$Me_3SiCH_2CH_2SO_2H$), 91 (24%, $C_7H_7^+$), 90 (100%, $Me_3SiNH_3^+$), 73 (42%, Me_3Si^+).

2-Methyl-4-phenyl-1-(2'-trimethylsilyl-1'-ethanesulfonyl)-2-butene (16). A solution containing 2-methyl-4-phenyl-3-(2'-trimethylsilyl-1'-ethanesulfonyl)-1-butene **(15)** (935mg, 3.01mmol) and BPO (150mg, 0.62mmol) in ^{t}BuOH (3ml) was heated at reflux temperature under argon for 72h. The solvent was evaporated

under reduced pressure and the residue was subjected to flash chromatography using ether / light petroleum (1:9 v/v) as the eluant to give 2-methyl-4-phenyl-1-(2'-trimethylsilyl-1'-ethanesulfonyl)-2-butene (**16**) (610mg, 1.96mmol, 65%). The *E* and *Z* isomers of the product were present in a ratio of approximately 3:1 as estimated from the ^{1}H n.m.r. spectrum of the crude product, and were partially resolved during chromatography so that samples of each isomer were obtained: *Z* isomer: Obtained as an oil; δ_H (500MHz; $CDCl_3$) 0.06 (9H, s, $(C\underline{H}_3)_3Si$), 1.09 (2H, m, $Me_3SiC\underline{H}_2CH_2SO_2$), 2.03 (3H, q, J=1.4Hz, $=CC\underline{H}_3$), 2.91 ($Me_3SiCH_2C\underline{H}_2SO_2$), 3.48 (2H, d, J=8Hz, $PhC\underline{H}_2$), 3.84 (2H, s, $=CC\underline{H}SO_2$), 5.86 (1H, tm, J=8Hz, $C\underline{H}=CCH_3$), 7.19-7.32 (5H, m, Ph); ν_{max} ($CHCl_3$) 1605, 1495, 1254, 1168, 1122cm^{-1}; *m/z* (CI, NH_3) 328 (7%, MNH_4^+), 145 (70%, MH^+-$Me_3SiCH_2CH_2SO_2H$), 144 (100%, M^+-$Me_3SiCH_2CH_2SO_2H$), 91 (23%, $C_7H_7^+$), 90 (68%, $Me_3SiNH_3^+$), 73 (61%, Me_3Si^+). *E* isomer: Obtained as an oil; (Found: C, 61.5; H, 8.5%. $C_{16}H_{26}O_2SSi$ requires: C, 61.9; H, 8.45%.); δ_H (500MHz; $CDCl_3$) 0.01 (9H, s, $(C\underline{H}_3)_3Si$), 1.01 (2H, m, $Me_3SiC\underline{H}_2CH_2SO_2$), 2.01 (3H, d, J=1Hz, $=CC\underline{H}_3$), 2.86 (2H, m, $Me_3SiCH_2C\underline{H}_2SO_2$), 3.47 (2H, d, J=7Hz, $PhC\underline{H}_2$), 3.68 (2H, s, $=CC\underline{H}_2SO_2$), 5.69 (1H, tm, J=7Hz, $C\underline{H}=CCH_3$), 7.16-7.32 (5H, m, Ph); δ_C (125.8MHz; $CDCl_3$) -2.09 ($(\underline{C}H_3)_3Si$), 8.56 ($Me_3Si\underline{C}H_2CH_2SO_2$), 16.93 ($=C\underline{C}H_3$), 34.72 ($Ph\underline{C}H_2$), 47.71 ($Me_3SiCH_2\underline{C}H_2SO_2$), 61.73 ($=C\underline{C}H_2SO_2$), 125.43 ($CH=\underline{C}CH_3$), 126.31 (Ph), 128.28 (Ph), 128.70 (Ph), 133.90 ($\underline{C}H=CCH_3$), 139.80 (Ph); ν_{max} ($CHCl_3$) 1603, 1495, 1313, 1254, 1121cm^{-1}; *m/z* (CI, NH_3) 328 (7%, MNH_4^+), 145 (57%, MH^+-$Me_3SiCH_2CH_2SO_2H$), 144 (24%, M^+-$Me_3SiCH_2CH_2SO_2H$), 91 (27%, $C_7H_7^+$), 90 (100%, $Me_3SiNH_3^+$), 73 (62%, Me_3Si^+).

Procedure for the desilylsulfonation of allylic 2-trimethylsilylethyl sulfones. The sulfone (*ca.* 1mmol) was dissolved in a few drops of dry THF under argon and the resulting solution was stirred in a bath at 15°C. Tetra-*n*-butylammonium fluoride (1M in THF; 1ml) was added and the solution was stirred for 2h. During this time the bath was allowed to warm to ambient temperature (22°C). Water (10ml) was added, the solution was extracted with ether (3x25ml), then the combined organic extracts were washed with water (10ml), dried ($MgSO_4$), filtered, and evaporated. The crude alkene was then purified by flash chromatography using light petroleum as the eluant. The following alkenes were prepared by this method:

3-Methyl-1-phenyl-2-butene (11). Prepared by desilylsulfonation of 2-methyl-4-phenyl-3-(2'-trimethylsilyl-1'-ethanesulfonyl)-1-butene (**15**) (324mg, 1.04mmol). The crude product was subjected to flash chromatography using light petroleum as the eluant to give 3-methyl-1-phenyl-2-butene (**11**) (95mg, 0.65mmol, 63%) as an oil; data as above.

2-Methyl-4-phenyl-1-butene (14). Prepared by desilylsulfonation of 2-methyl-4-phenyl-1-(2'-trimethylsilyl-1'-ethanesulfonyl)-2-butene (**16**) (367mg, 1.18mmol). The crude product was subjected to flash chromatography using light petroleum as the eluant to give 2-methyl-4-phenyl-1-butene (**14**) (96mg, 0.66mmol, 56%) as an oil; data as above

2-(2'-Methyl-2'-propenylthio)benzothiazole. Methallyl chloride (9.9ml, 9.1g, 100.3mmol) was added portionwise over 15min to a mixture of 2-mercaptobenzothiazole (16.7g, 99.9mmol) and sodium methoxide (5.37g, 99.4mmol) in methanol (120ml) stirred at room temperature under nitrogen After 3.5h at room temperature the brown solution was heated under reflux for 15min then allowed to cool. Water (120ml) was added, the mixture was extracted into toluene (2x100ml) and the combined organic extracts were then washed with aqueous sodium hydroxide (2M, 100ml), dilute hydrochloric acid (1M, 100ml) and brine (100ml), dried

($MgSO_4$), filtered, and evaporated to give 2-(2'-methyl-2'-propenylthio)benzothiazole (20.8g, 93.9mmol, 94%) as an orange oil; δ_H (200MHz; $CDCl_3$) 1.92 (3H, s, =CC$\underline{H}_3$), 4.03 (2H, s, C$\underline{H}_2$SBt), 4.99 (1H, s, =C$\underline{H}$), 5.14 (1H, s, =C$\underline{H}$), 7.31 (1H, t, J=8Hz, Bt$\underline{H}$), 7.43 (1H, t, J=8Hz, Bt$\underline{H}$), 7.78 (1H, d, J=8Hz, Bt$\underline{H}$), 7.90 (1H, d, J=8Hz, Bt$\underline{H}$). The product was used without purification in the next stage.

2-(2'-Methyl-2'-propenesulfonyl)benzothiazole (17). A solution of ammonium molybdate (vi) tetrahydrate (3.98g, 3.22mmol) in aqueous hydrogen peroxide (30% w/w; 30.6g, 296mmol) was added portionwise over 10min to a solution of 2-(2'-methyl-2'-propenylthio)benzothiazole (18.74g, 84.7mmol) in ethanol (400ml) stirred at 0°C. After 6.5h stirring at 0°C, the solution was then allowed to stand at -4°C for 16h. The solution was then evaporated under reduced pressure at room temperature and the residue was dissolved in dichloromethane (50ml) and washed with dilute sulfuric acid (2M, 100ml). The aqueous phase was extracted into dichloromethane (3x60ml), and the combined organic extracts were washed with brine (100ml), dried ($MgSO_4$), filtered, and evaporated leaving a pale orange solid which was recrystallised from dichloromethane / ethanol to give 2-(2'-methyl-2'-propenesulfonyl)benzothiazole **(17)** (18.17g, 71.7mmol, 85%) as off-white crystals; m.p. 96-97°C (lit.[19] 93-94°C); δ_H (200MHz; $CDCl_3$) 1.97 (3H, s, =CC$\underline{H}_3$), 4.23 (2H, s, C$\underline{H}_2SO_2$Bt), 4.93 (1H, s, =C$\underline{H}$), 5.14 (1H, s, =C$\underline{H}$), 7.64 (2H, m, Bt$\underline{H}$), 8.03 (1H, d, J=8Hz, Bt$\underline{H}$), 8.26 (1H, d, J=8Hz, Bt$\underline{H}$).

2-(2'-Methyl-4'-phenyl-1'-butene-3'-sulfonyl)benzothiazole (18). A solution of LDA [prepared at 0°C from ^{n}BuLi (11.1mmol), and dry ^{i}Pr$_2$NH (1.70ml, 1.23g, 12.1mmol) in dry THF (20ml), then allowed to warm to room temperature] was added dropwise over 10min, using a cannula, to a solution of 2-(2'-methyl-2'-propenylthio)benzothiazole **(17)** (2.00g, 7.89mmol) in THF (20ml) stirred under nitrogen at -78°C. After 30min, benzyl bromide (2.82ml, 4.06g, 23.7mmol) was added, then the solution was allowed to warm to room temperature over 3h. The reaction was quenched by the cautious addition of water (40ml). The solution was then extracted using dichloromethane (3x40ml). The combined organic extracts were washed with dilute hydrochloric acid (1M, 2x40ml), water (40ml), and brine (40ml) then dried (MgSO4), filtered, and evaporated to give an orange oil which partially crystallised upon standing at -4°C. The product was triturated with light petroleum to remove excess benzyl bromide, then recystallised from ethyl acetate / light petroleum (b.p. 60-80°C) to give 2-(2'-methyl-4'-phenyl-1'-butene-3'-sulfonyl)benzothiazole **(18)** (1.65g, 4.80mmol, 61%) as a pale brown solid; m.p. 114-116°C; (Found: C, 62.45; H, 4.9. $C_{18}H_{17}NO_2S_2$ requires: C, 62.95; H, 5.0%); δ_H (200MHz; $CDCl_3$) 1.83 (3H, s, =CC$\underline{H}_3$), 3.18-3.66 (2H, ABX, J_{AX}=4Hz, J_{BX}=12Hz, J_{AB}=15Hz, C$\underline{H}_2$Ph), 4.56 (1H, dd, ABX, C$\underline{H}$CH$_2$Ph), 5.00 (1H, s, =C$\underline{H}$), 5.10 (1H, s, =C$\underline{H}$), 7.25 (5H, m, Ph), 7.65 (2H, m, Bt$\underline{H}$), 8.04 (1H, d, J=8Hz, Bt$\underline{H}$), 8.27 (1H, d, J=10Hz, Bt$\underline{H}$); δ_C (50.3MHz; $CDCl_3$) 20.8 (C$\underline{H}_3$), 32.2 (C$\underline{H}_2$Ph), 72.2 (C$\underline{H}$CH$_2$Ph), 122.5 (CMe=C$\underline{H}_2$), 125.7 (C$\underline{M}$e=CH$_2$), 127.1 (Ar), 127.8 (Ar), 128.2 (Ar), 128.8 (Ar), 129.1 (Ar), 136.3 (Ar).

2-(2'-Methyl-4'-phenyl-2'-butene-1'-sulfonyl)benzothiazole (19). A mixture containing 2-(2'-methyl-4'-phenyl-1'-butene-3'-sulfonyl)benzothiazole **(18)** (1.72g, 5.01mmol), and BPO (0.24g, 0.99mmol) in tBuOH (5ml) was heated to reflux temperature, which resulted in the formation of a homogenous solution. After heating under reflux for 22h, the solution was evaporated and the residue was flash chromatography using ether / isohexane (1:9-1:4 v/v) as the eluant to give 2-(2'-methyl-4'-phenyl-2'-butene-1'-sulfonyl)benzothiazole **(19)** (1.34g, 3.90mmol, 78% yield) as a colourless solid (*E/Z* ratio estimated as approximately 7:2 by ^{1}H n.m.r.); δ_H

(300MHz; $CDCl_3$) 1.99 (3H, m, =CC$\underline{H}_3$), 3.30 (2H, m, C$\underline{H}_2$Ph), 4.21 (2H, s, C$\underline{H}_2SO_2$, *E* isomer), 4.38 (2H, s, C$\underline{H}_2SO_2$, *Z* isomer), 5.51 (1H, t, C=C$\underline{H}$CH$_2$Ph, *E* isomer), 5.79 (1H, t, C=C$\underline{H}$CH$_2$Ph, *Z* isomer), 6.81-7.19 (5H, m, Ph), 7.61 (2H, m, Bt$\underline{H}$), 7.96 (1H, m, Bt$\underline{H}$), 8.18 (1H, m, Bt$\underline{H}$). In a separate experiment, recrystallisation [ethyl acetate / light petroleum (b.p. 60-80°C)] of the crude product gave the pure *E* isomer; m.p. 96.5-97.5°C; (Found: C, 63.1; H, 4.9. $C_{18}H_{17}NO_2S_2$ requires: C, 62.95; H, 5.0%); δ_H (200MHz; $CDCl_3$) 1.99 (3H, m, =CC$\underline{H}_3$), 3.30 (2H, d, J=8Hz, C$\underline{H}_2$Ph), 4.22 (2H, s, C$\underline{H}_2SO_2$), 5.53 (1H, t, J=8Hz, C=C$\underline{H}$CH$_2$Ph), 6.83 (2H, m, Ph), 7.07 (3H, m, Ph), 7.62 (2H, m, Bt$\underline{H}$), 7.97 (1H, m, Bt$\underline{H}$), 8.20 (1H, m, Bt$\underline{H}$).

Procedure for the desulfonation of allylic 2-benzothiazolyl sulfones. The sulfone was dissolved in THF (2mlmmol^{-1}). Sodium cyanoborohydride (5eq.) was added followed by a few drops of dilute aqueous hydrochloric acid (2M, ca. 50µlmmol^{-1}). After 5h at room temperature, a further portion of dilute hydrochloric acid was added, then the solution was stirred at room temperature for 3 days. The solution was then diluted with ether, and the organic layer was washed with aqueous sodium hydroxide and brine, then dried ($MgSO_4$), filtered, and evaporated. The crude alkene was then purified by flash chromatography using light petroleum as the eluant. The following alkenes were prepared by this method:

3-Methyl-1-phenyl-2-butene (11). Prepared by desulfonation of 2-(2'-methyl-4'-phenyl-1'-butene-3'-sulfonyl)benzothiazole **(18)** (512mg, 1.49mmol). The crude product was subjected to flash chromatography using isohexane as the eluant to give 3-methyl-1-phenyl-2-butene **(11)** (183mg, 1.25mmol, 84%) as an oil; data as above.

2-Methyl-4-phenyl-1-butene (14). Prepared by desilylsulfonation of 2-(2'-methyl-4'-phenyl-2'-butene-1'-sulfonyl)benzothiazole **(19)** (253mg, 0.75mmol). The crude product was subjected to flash chromatography using isohexane as the eluant to give 2-methyl-4-phenyl-1-butene **(14)** (68.3mg, 0.47mmol, 63%) as an oil; data as above.

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