Radical-induced 1,3-Rearrangements of Allylic Sulfones bearing an Alkylthio or Arylthio Substituent at the α-Position

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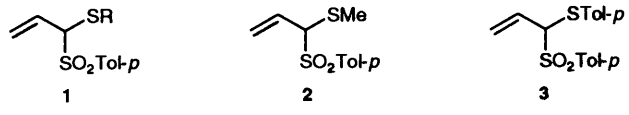
1-Methylthio-1-*p*-tolylsulfonylprop-2-ene **2** underwent 1,3-rearrangement under conditions of radical initiation with migration of the *p*-tolylsulfonyl group by a process considered to have involved addition–elimination of arylsulfonyl radicals. In contrast, the reaction of 1-*p*-tolylthio-1-*p*-tolylsulfonylprop-2-ene **3** under similar conditions gave scrambled products, indicating that arylthio and arylsulfonyl radicals participate with about equal efficiency.

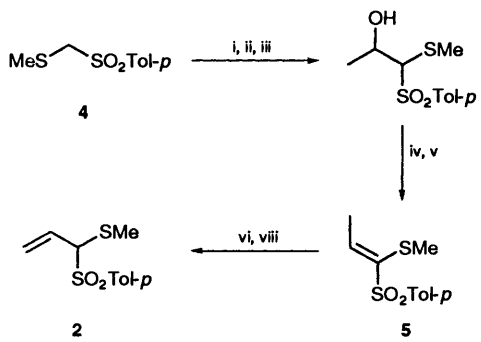
Previous work, both by ourselves and other investigators,[1] has shown that appropriately substituted allylic sulfones can undergo 1,3-rearrangements under two main types of conditions related to two mechanistic extremes. One type, occurring under conditions of radical initiation, characteristic of fairly lightly alkyl-substituted systems is considered to involve addition–elimination of alkyl- or aryl-sulfonyl radicals (a S_H2' process). The other type, occurring under ionising conditions, characteristic of systems fairly heavily substituted with alkyl or other cation-stabilising groups appears to proceed by dissociation–recombination involving allyl cation/sulfinate ion-pairs.

It is also known that allylic sulfides undergo 1,3-rearrangement under radical conditions by a S_H2' process,[2] and we became interested in investigating the reactions of compounds of type **1** where the possibility exists for migration of the thio and/or the sulfonyl group. The present paper describes the preparation of 1-methylthio-1-*p*-tolylsulfonylprop-2-ene **2** and of 1-*p*-tolylthio-1-*p*-tolylsulfonylprop-2-ene **3**, and a study of their behaviour under rearrangement conditions.



1 **2** **3**

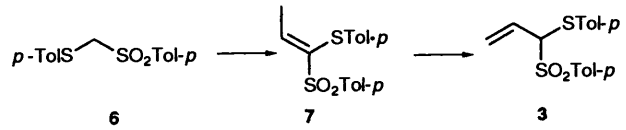
Although 1-methylthio-1-*p*-tolylsulfonylprop-2-ene **2** is a known compound which had been prepared, in low conversion, by photoisomerisation of 1-methylthio-3-*p*-tolylsulfonylprop-1-ene,[3] the method of preparation was not suitable for obtaining reasonable quantities of **2**. A new preparation of **2** was therefore devised, based, except for the last stages, on known chemistry,[4] starting from methylthiomethyl *p*-tolyl sulfone[5] **4** (Scheme 1). The key step was the 'deconjugation' of the vinyl sulfone **5** to give **2**. This was achieved by treatment of **5** with lithium d-isopropylamide (LDA) followed by quenching of the presumed intermediate allylic anion with acetic acid at low temperature. That **2** was indeed the kinetically controlled product of α-protonation of the intermediate anion was corroborated by the observation that treatment of **2** with triethylamine led to complete reversion to the more stable isomer **5**.



4 **2** **5**

Scheme 1 *Reagents and conditions:* i, BuLi, THF, −78 °C; ii, MeCHO; iii, AcOH; iv, Ac_2O, DMAP, Py, 20 °C, 20 h; v, H_2O; vi, LDA, THF, −78 °C; vii, AcOH

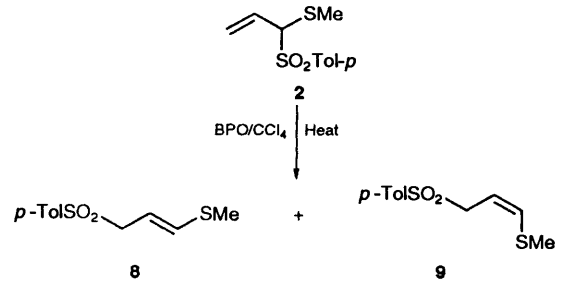
For the preparation of 1-*p*-tolylthio-1-*p*-tolylsulfonylprop-2-ene **3** in an analogous way to that employed above for **2**, *p*-tolyl *p*-tolylthiomethyl sulfone **6** was required. This compound was obtained from bis-*p*-tolylthiomethane using the two-step oxidation procedure developed by Jackson *et al.* for the phenyl analogue.[4] Elaboration of **6** to the vinyl sulfone **7** proceeded uneventfully, but 'deconjugation' to give the allylic isomer **3** did not work using LDA, other products being formed that were not further investigated. Fortunately, the use of lithium bistrimethylsilylamide circumvented the problem.



6 **7** **3**

The sulfonyl sulfide **2** was subjected to radical rearrangement conditions using dibenzoyl peroxide (BPO) in carbon tetrachloride under reflux. The two products, detected in the ^1H NMR spectra of the crude material and isolated by chromatography, were (*E*)- and (*Z*)-3-methylthioallyl *p*-tolyl sulfone **8** and **9**, readily identified by comparison with literature data for the authentic compounds.[6] Conversions found varied between 73 and 60%, and the ratio of *E* to *Z* isomers obtained varied from 2.3:1 to 1.8:1. Submission of each of the isomers (**8** and **9**) to the reaction conditions resulted, in both cases, in a mixture in which none of the allylic sulfonyl sulfide **2** was detected by ^1H NMR spectroscopy, but which contained only the *Z* and *E* isomers of **8** and **9**, in a *Z*:*E* ratio 1.0:1.0 (starting from the *Z* isomer **9**) and 0.45:1.0 (starting from the *E* isomer **8**). These results suggest that the equilibrium position to which the rearrangement between **2**, **8** and **9** tends is a mixture containing **8** and **9** in ratio 2:1, and no **2**, but that this equilibrium is never actually quite attained under the reaction conditions (Scheme 2), owing to inefficient propagation of the radical chain.

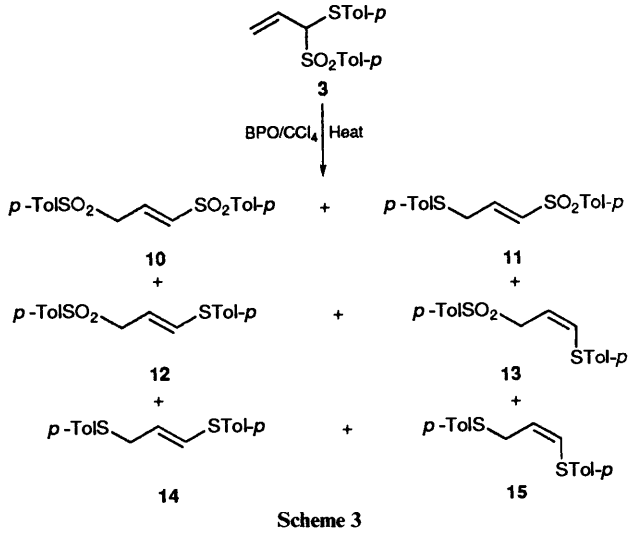
It thus appears that rearrangement of **2** under radical conditions occurs by a clean 1,3-shift of the *p*-tolylsulfonyl group involving addition–elimination of *p*-$TolSO_2^{\bullet}$. However, since it is known[6] that 3-alkylthioprop-1-enyl *p*-tolyl sulfones are thermodynamically less stable than the vinyl sulfide isomers



Scheme 2

such as **8** and **9** and are readily isomerised to them under mildly basic conditions, the possibility exists of rearrangement by 1,3-shift of the methylthio group followed by a 1,3-prototropic shift. The latter possibility was excluded by an experiment (see Experimental section) in which α-deuteriated **2** was subjected to the rearrangement conditions and gave products **8** and **9** containing deuterium only in the α-position to the thiomethyl substituent. We conclude, therefore, that radical-induced rearrangement of **2** involves preferential migration of the tolylsulfonyl group.

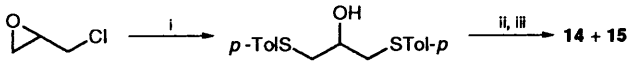
The *p*-tolylthio substituted sulfone **3** was also subjected to rearrangement conditions analogous to those used for **2** (BPO/CCl_4/reflux). In this case a more complex set of products was obtained corresponding to those expected for migration of both *p*-tolylthio and *p*-tolylsulfonyl groups (Scheme 3). A



Scheme 3

control experiment in the absence of BPO resulted in recovery of starting material.

Compounds **10**, **11**, **12** and **13**, known compounds, were identified by spectroscopic comparison with literature data. Structures of compounds **14** and **15** were assigned by comparison with authentic materials prepared by another route as summarised in Scheme 4. The rearrangement of **3** was essentially complete after 48 h under the conditions used and the

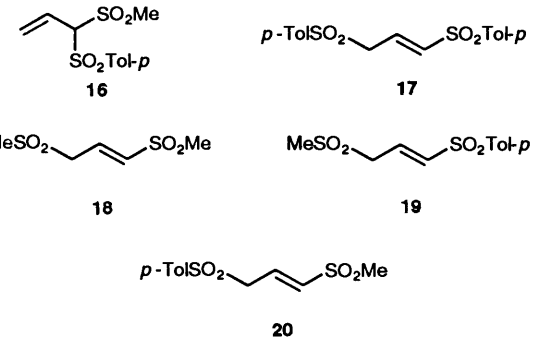


Scheme 4 *Reagents and conditions:* i, *p*-TolSH, KOH; ii, TsCl–Py; iii, DBU, PhMe, 110 °C

relative proportions of products formed, relative to **12** were: **10** 0.68, **11** 0.27, **12** 1.00, **13** 0.88, **14** 0.24 and **15** 0.14. These ratios were determined from the relative intensities of the doublets for the methylene hydrogens of the products in the ^1H NMR spectrum of the crude product. Monitoring at appopriate intervals of time by ^1H NMR showed that the relative proportion of products did not change during the course of the reaction. The formation of only the *E* isomers of the vinyl sulfones **10** and **11** but both the *E* and *Z* isomers of the vinyl sulfides **12**/**13** and **14**/**15** is expected in terms of known stabilities of vinyl sulfones and vinyl sulfides,[7] and explicable in terms of the much greater steric demands of the sulfone as compared to the sulfide group.

The identity of the products and the nature of the conditions make it highly likely that the reaction (Scheme 3) occurs by addition–elimination involving both *p*-TolS$^\bullet$ and *p*-TolSO$_2^\bullet$ radicals. In particular, the formation of the bis-sulfone **10** and the bis-sulfides **14** and **15** would be difficult to explain simply in any other way. Thus bis-sulfone **10** is considered to have been formed by addition of *p*-TolSO$_2^\bullet$ to **3** followed by elimination of *p*-TolS$^\bullet$ *etc.* This outcome thus stands in contrast to that of the methylthio substituted sulfone **2** where only addition–elimination of *p*-TolSO$_2^\bullet$ occurred. Because of the very nature of radical-chain reactions it is difficult to be precise about the reasons for this difference and one has, for example, to consider not only the relative rates of addition of *p*-TolS$^\bullet$ *versus* *p*-TolSO$_2^\bullet$ to **3** but also the relative rates of elimination of the same two radicals from the initial adduct radical(s). Furthermore, the relative rates of elimination will depend not only on the intrinsic leaving group abilities of the two radicals but also on the stabilities of the vinyl sulfone or vinyl sulfide products, particularly given the fact[7,8] that the sulfide substituent is much more double-bond stabilising than the sulfone substituent. An important study by Wagner and coworkers[9] on the irradiation of appropriately δ substituted valerophenones led to a determination of the relative rates of elimination of sulfur-centred radicals. Their results gave the following values for k_{rel}: BuS$^\bullet$ 0.16, PhS$^\bullet$ 110 and PhSO$_2^\bullet$ 6.8. Radical leaving group abilities thus appear to increase in the sequence AlkylS$^\bullet$ < ArylSO$_2^\bullet$ < ArylS$^\bullet$, presumably the difference between AlkylS$^\bullet$ and ArylS$^\bullet$ reflects the fact that the former is a σ-radical while the latter is a π-radical. It seems likely that the main reason for the difference between the outcome of the rearrangement of the methylthio substituted sulfone **2** and of the *p*-tolylthio substituted sulfone **3** is this nearly 700 fold greater leaving group ability of ArylS$^\bullet$ *versus* AlkylS$^\bullet$ from the relevant β-thiosubstituted radical. In the comparison between ArylSO$_2^\bullet$ and ArylS$^\bullet$, relevant to the case of the sulfone **3**, the leaving group ability difference is not so great (16 fold); this factor does not dominate and, in fact, products derived by loss of ArylSO$_2^\bullet$ (**12**–**15**) predominate over those derived by loss of ArylS$^\bullet$ (**10** and **11**). A study by Ueno and coworkers[10] on tributyltin hydride reduction of α-disubstituted benzophenones with various sulfur substituents, which also showed a clear preference for β-elimination of PhS$^\bullet$ in intramolecular competition with PhSO$_2^\bullet$, is relevant. Clearly, our results indicate that in the case of **3** the other influences mentioned above play a significant rôle.

For comparison purposes we decided to investigate the outcome of attempted rearrangement of the bis-sulfone **16** derived by oxidation of the thiomethyl sulfone **2** with OXONE® (potassium peroxymonosulfate). Owing to the insolubility of **16** in carbon tetrachloride it was necessary to carry out the reaction in refluxing chloroform containing BPO (10 mol%). Under these conditions reaction was 90% complete after 18 h. Products obtained were the four bis-sulfones **17**, **18**, **19** and **20** in the ratio 1.0:0.7:0.9:0.9; structures were assigned on the basis of ^1H NMR spectroscopic evidence. Only *E* isomers of the products were found as expected from earlier considerations. A 1 : 1 mixture of the two isomeric bis-sulfones **19** and **20** remained unchanged after submission to the reaction conditions even after 72 h and no further equilibration to give either **17** or **18** occurred. In the case of **16**, apparently, addition



of $MeSO_2^{\bullet}$ and p-$TolSO_2^{\bullet}$ and elimination of $MeSO_2^{\bullet}$ and p-$TolSO_2^{\bullet}$ are all about equally likely thus leading to the fairly evenly scrambled mixture of products.

Experimental

^1H NMR spectra were recorded on Varian Gemini (200 MHz) or Bruker AM500 (500 MHz) spectrometers; J values are given in Hz; the aromatic AA'BB' system of p-tolyl groups is quoted as if it were two sets of doublets. ^{13}C NMR spectra were recorded on Varian Gemini 200 at 50.2 MHz and chemical shifts are quoted in ppm downfield from TMS. Ether refers to diethyl ethers.

2-Hydroxy-1-methylthiopropyl p-*Tolyl Sulfone*.—A solution of methylthiomethyl p-tolyl sulfone[5] (10.8 g, 50 mmol) in dry THF (100 cm^3) was cooled in an acetone–solid carbon dioxide slush bath, and butyllithium (1.6 mol dm^{-3} solution in hexane; 31.3 cm^3, 50 mmol) was added to it by syringe with stirring. After 30 min, acetaldehyde (16% w/v solution in dry THF; 20 cm^3, 73 mmol) was added by syringe to the mixture which was stirred for a further 2 h before being quenched by the addition of acetic acid (20 cm^3). The mixture was allowed to warm to room temperature after which it was diluted with ether (100 cm^3) and washed with aq. HCl (100 cm^3), aq. NaOH (100 cm^3) and brine (100 cm^3). The washings were combined and extracted with ether (2 × 75 cm^3); these ethereal extracts were then washed as before (50 cm^3 each washing agent) and added to the original solution. The solution was dried ($MgSO_4$), filtered and evaporated under reduced pressure to give an oil (13.7 g) as a mixture of two diastereoisomers in the ratio 1 : 1.3; δ_H(200 MHz, $CDCl_3$) 7.84 (2 H, d, Ar, both isomers), 7.36 (2 H, d, Ar, both isomers), 4.60 (1 H, br q, J 6.3, 2-H, isomer 2), 4.33 (1 H, qn, J 6.3, 2-H, isomer 1), 3.81 (1 H, d, J 6.4, 1-H, isomer 1) 3.64 (1 H, d, J 1.2, 1-H, isomer 2), 3.26 (1 H, br s, OH, both isomers), 2.43 (3 H, s, MeC_6H_4, both isomers), 2.07 (3 H, s, SCH_3, isomer 1), 2.02 (3 H, s, SCH_3, isomer 2) 1.36 (3 H, d, 6.3, 3-H, isomer 1) and 1.35 (3 H, d, 6.3, 3-H, isomer 2).

1-Methylthioprop-1-enyl p-*Tolyl Sulfone* **5**.—In a typical procedure, dimethylaminopyridine (9.4 g, 0.077 mol) was dissolved in a solution of 2-hydroxy-1-methylthiopropyl p-tolyl sulfone (20 g, 0.076 mol) in pyridine (300 cm^3) and acetic anhydride (73 cm^3, 0.661 mol) was added over 10 min to the stirred solution, with cooling (ice-bath). The resulting solution was stirred for 20 h at 18 °C, and then quenched by the addition of water (50 cm^3) with cooling (ice-bath). Ether (300 cm^3) was added to the mixture which was then washed with aq. HCl (2 × 300 cm^3) aq. Na_2CO_3 (300 cm^3) and brine (300 cm^3), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The resulting dark brown crystals were dissolved in ether and the solution passed through a short silica column, washing the column through with more ether. The eluent was evaporated under reduced pressure and the residue recrystallised (ether–light petroleum) to give the product as pale orange crystals (14.5 g, 69%), m.p. 71–72.5 °C (lit.,[3] 72–73 °C); δ_H(200 MHz, $CDCl_3$) 7.82 (2 H, d, Ar), 7.61 (1 H, q, J 6.9, 2-H), 7.33 (2 H, d, Ar), 2.44 (3 H, s, $CH_3C_6H_4$), 2.21 (3 H, s, SCH_3) and 2.10 (3 H, d, J 6.9, 3-H).

1-Methylthioallyl p-*Tolyl Sulfone* **2**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 9.3 cm^3, 14.9 mmol), followed by dry THF (30 cm^3), were added by syringe with stirring to diisopropylamine (3.3 cm^3, 2.4 g, 23.5 mmol); the resulting solution was cooled in an acetone–solid carbon dioxide slush bath. 1-Methylthioprop-1-enyl p-tolyl sulfone (3.0 g, 12.4 mmol) dissolved in dry THF (30 cm^3) was added *via* a needle tube, to the solution which was then stirred for 15 min before being quenched by the addition to it of acetic acid (15 cm^3). The mixture was allowed to warm to 18 °C and then diluted with ether (75 cm^3), washed with aq. HCl (75 cm^3), aq. Na_2CO_3 (75 cm^3) and brine (75 cm^3), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The residue, purified by flash chromatography, was applied in dichloromethane and eluted with ether–light petroleum (b.p. 30–40 °C) (1 : 3 v/v). Recrystallisation [ether–light petroleum (b.p. 40–60 °C)] gave the product as white crystals (2.2 g, 73%), m.p. 67–68 °C (lit.,[3] 66.5–67 °C); δ_H(200 MHz, $CDCl_3$) 7.79 (2 H, d, Ar), 7.34 (2 H, d, Ar), 5.74–5.92 (1 H, m, 2-H), 5.38 (1 H, d, J 10.4, 3-H'), 5.30 (1 H, d, J 17.0, 3-H''), 4.37 (1 H, d, J 8.4, 1-H), 2.45 (3 H, s, MeC_6H_4) and 2.36 (3 H, s, SCH_3). Attempts to substitute other secondary amines (dicyclohexylamine, *N*-isopropylcyclohexylamine, 2,2,6,6-tetramethylpiperidine and 1,1,1,3,3,3-hexamethyldisilazane) for the diisopropylamine resulted either in incomplete isomerisation or in intractable products.

p-*Tolyl* p-*Tolylthiomethyl Sulfone* **6**.—A mixture of dichloromethane (500 cm^3) and triethylamine (55 cm^3) were purged with nitrogen for 30 min and then stirred and cooled in an ice bath. p-Thiocresol (49.7 g, 0.4 mol) dissolved in dichloromethane (250 cm^3) was then added dropwise to the mixture over 30 min after which the latter was allowed to warm to 18 °C. After the mixture had been stirred for 3.5 h the triethylamine hydrochloride was removed by filtration through a sintered glass funnel, and the filtrate was washed with aq. NaOH (10%, 2 × 100 cm^3), aq. HCl (2 mol dm^{-3}; 2 × 100 cm^3) and water (150 cm^3). The dichloromethane solution was dried ($MgSO_4$) and evaporated under reduced pressure.

The crude thiocetal was heated under reflux with a stirred solution of NaOH (8.8 g, 0.22 mol) in DMSO (40 cm^3) and water (40 cm^3) for 1 h and then allowed to cool. The mixture was extracted with toluene (100 cm^3), and the combined extracts were washed with hydrochloric acid (2 mol dm^{-3}) and water (100 cm^3 each), dried ($MgSO_4$), and evaporated under reduced pressure to yield bis(p-tolylthio)methane (34.6 g, 66.4%), δ_H(200 MHz) 7.42 (4 H, d, J 8, Ar), 7.20 (4 H, d, J 8, Ar), 4.34 (2 H, s, SCH_2S) and 2.41 (6 H, s, Me).

A solution of the thioacetal (29.37 g, 113 mmol) in acetic acid (84 cm^3) was cooled in a cold water-bath and hydrogen peroxide (30% aqueous solution; 19 cm^3, 167 mmol) was added to it with stirring. After the mixture had warmed to 18 °C, stirring was continued for 60 min. Sufficient sodium metabisulfite (10% aqueous solution) was then added to the mixture so that it no longer turned starch–iodide paper black; dichloromethane (560 cm^3) and water (130 cm^3) were then added to the mixture, followed by careful addition of potassium carbonate (105 g, 0.76 mol). After effervescence had ceased, the organic layer was extracted with dichloromethane (3 × 70 cm^3). The organic extracts were combined, dried and evaporated under reduced pressure. The residue was purified by dry flash column chromatography in several portions of *ca.* 5 g each to give p-tolyl p-tolylthiomethyl sulfoxide (70% yield on average), δ_H(200

MHz) 7.59 (2 H, d, *J* 8.2, Ar), 7.35 (2 H, d, *J* 8.25, Ar), 7.30 (2 H, d, *J* 8.25, Ar), 7.12 (2 H, d, *J* 8.2, Ar), 4.16, 4.01 (2 H, ABq, *J* 13.2, SCH_2SO), 2.41 (3 H, s, Me) and 2.34 (3 H, s, Me).

p-Tolyl *p*-tolylthiomethyl sulfoxide (4.63 g, 16.8 mmol) was dissolved in acetone (80 cm^3) and water (3 cm^3), and the solution cooled in an ice-bath. Potassium permanganate (2.7 g, 17.1 mmol) was then added to the stirred solution in several portions. The resulting mixture was warmed to 18 °C, and stirring was continued for 1 h. The insoluble matter was filtered off through Celite on a sintered glass funnel and the filtrate was evaporated under reduced pressure. The residue was dissolved in dichloromethane (40 cm^3) and aqueous sodium metabisulfate (10%) was added to the solution until it became colourless. The aqueous layer was extracted with dichloromethane and the extracts were dried and evaporated under reduced pressure. Crystallisation of the residue from ether–light petroleum (b.p. 40–60 °C) yielded *p*-tolyl *p*-tolylthiomethyl sulfone (3.35 g, 68%), m.p. 77 °C (lit.,[11] 75–76 °C); δ_H(200 MHz) 7.79 (2 H, d, *J* 8.25, Ar), 7.32 (2 H, d, *J* 6.7, Ar), 7.28 (2 H, d, *J* 6.7, Ar), 7.06 (2 H, d, *J* 8.2, Ar), 4.28 (2 H, s, SO_2CH_2S), 2.45 (3 H, s, Me) and 2.32 (3 H, s, Me).

p-*Tolyl* 1-p-*Tolylthioprop*-1-*enyl Sulfone* **7**.—A solution of *p*-tolyl *p*-tolylthiomethyl sulfone (2.04 g, 6.98 mmol) in dry THF (36 cm^3) was cooled in an acetone–solid CO_2 slush bath to −78 °C and BuLi (1.58 mol dm^{-3} solution in hexane; 5.6 cm^3, 8.96 mmol) was added to it with stirring. After the mixture had warmed to 0 °C (30 min) the acetone–solid CO_2 slush bath was removed; acetaldehyde [15.5% solution in dry THF (wt/wt); 3 cm^3, 10.6 mmol) was added to the mixture which was then stirred for 30 min. After this, acetic acid (3 cm^3) was added to the mixture followed by diethyl ether (36 cm^3). The mixture allowed to warm to 18 °C and then washed with aq. HCl, aq. NaOH, water and brine (all 25 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give 2-hydroxy-1-*p*-tolylthiopropyl *p*-tolyl sulfone (2.35 g, 100%); it comprised a mixture of two diastereoisomers in the ratio 1 : 1, δ_H(200 MHz) 7.81 (2 H, d, *J* 8.3, Ar) 7.73 (2 H, d, *J* 8.3, Ar) 7.31 (2 H, d, Ar) 7.27 (2 H, d, Ar) 6.97 (4 H, br s, Ar) 4.82 (1 H, br q, *J* 6.4, 2-H, isomer 2) 4.53 (1 H, qn, *J* 6.3, 2-H, isomer 1) 4.19 (1 H, d, *J* 6.3, 1-H, isomer 1) 4.03 (1 H, d, *J* 1.2, 1-H, isomer 2) 2.45 (3 H, s, MeC_6H_4, both isomers) 2.29 (3 H, s, MeC_6H_4, both isomers) 1.53 (3 H, d, *J* 6.32, 3-H, isomer 2) and 1.52 (3 H, d, *J* 6.32, 3-H, isomer 1).

4-Dimethylaminopyridine (DMAP) (2.36 g, 19.3 mmol) was added to a solution of 2-hydroxy-1-*p*-tolylthiopropyl *p*-tolyl sulfone (6.39 g, 19.0 mmol) in pyridine (75 cm^3) followed by acetic anhydride (18 cm^3, 16 mol) added over 10 min with cooling (ice bath); the mixture was then stirred at 18 °C for 24 h after which it was diluted with water (13 cm^3) followed by ether (75 cm^3) and then washed with aq. HCl (2 × 75 cm^3), aq. Na_2CO_3 (74 cm^3) and brine (75 cm^3). The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure and the resulting dark brown crystals were dissolved in ether and the solution passed through a short silica column; after the column had been washed through with further ether, the eluent was evaporated under reduced pressure. Recrystallisation of the residue from ether–light petroleum (b.p. 40–60 °C) yielded the *sulfone* **7** as off-white crystals (3.38 g, 63%), m.p. 90 °C (Found: C; 64.3; H, 5.9. $C_{17}H_{18}O_2S_2$ requires C, 64.1; H, 5.7%); δ_H(200 MHz) 7.80 (1 H, q, *J* 6.0, 2-H), 7.79 (2 H, d, *J* 8.0, Ar), 7.24 (2 H, d, *J* 8.0, Ar) 6.96 (4 H, br s, Ar), 2.40 (3 H, s, $CH_3C_6H_4$), 2.28 (3 H, s, MeC_6H_4) and 2.04 (3 H, d, *J* 6.9, 3-H).

p-*Tolyl* 1-p-*Tolylthioallyl Sulfone* **3**.—*p*-Tolyl 1-*p*-tolylthioprop-1-enyl sulfone (0.49 g, 1.54 mmol) was dissolved in THF (15 cm^3) and the solution cooled in an acetone–solid CO_2 slush bath under nitrogen. Lithium bis(trimethylsilyl)amide (1 mol dm^{-3} solution in THF; 2.3 cm^3, 2.3 mmol) was added to the reaction mixture which was then stirred for 10 min before acetic acid (8 cm^3) was added to it. After 5 min, ether (40 cm^3) was added to the mixture which was then allowed to warm to 18 °C. The organic layer was separated, washed with aq. HCl, aq. Na_2CO_3, brine and water (all 40 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The resulting yellow crystals were recrystallised from ether–light petroleum (b.p. 40–60 °C) to yield the *sulfone* **3** (0.295 g, 60%), m.p. 95 °C (Found: C, 64.3; H, 5.65. $C_{17}H_{18}O_2S_2$ requires C, 64.1; H, 5.7%); δ_H(200 MHz) 7.79 (2 H, d, Ar), 7.37 (2 H, d, Ar), 7.33 (2 H, d, Ar), 7.10 2 H, d, Ar), 5.93–5.75 (1 H, m, 2-H), 5.36 (1 H, d, *J* 10.1, 3-H), 5.27 (1 H, d, *J* 16.8, 3-H), 4.61 (1 H, d, *J* 8.63, 1-H), 2.46 (3 H, s, $CH_3C_6H_4$) and 2.34 (3 H, s, MeC_6H_4).

Base-catalysed Rearrangement of p-*Tolyl* 1-p-*Tolylthioallyl Sulfone* **3**.—The sulfone **3** (25 mg, 0.079 mmol) was dissolved in $CDCl_3$ (0.5 cm^3) and triethylamine (0.0081 g, 0.08 mmol) was added to the solution. The resulting mixture was placed in an NMR tube, and spectra taken at intervals. After 4 h, all starting material had been transformed, leaving as the only product the sulfone **7** (see earlier for NMR data).

Rearrangement of 1-*Methylthioallyl* p-*Tolyl Sulfone* **2**.—The sulfone **2** (0.6 g, 2.47 mmol) and dibenzoyl peroxide (0.06 g, 0.25 mmol, 10 mol%) were dissolved in carbon tetrachloride (50 cm^3) and the solution heated under reflux at 90 °C for 16 h. After cooling to room temperature, the solution was washed with aq. NaOH (50 cm^3), aq. sodium metabisulfite (50 cm^3), aq. HCl (50 cm^3) and water (50 cm^3), dried ($CaCl_2$) filtered and evaporated under reduced pressure to give an oil shown by ^1H NMR spectroscopy to consist of starting material, and (*Z*)- and (*E*)-3-methylthioallyl *p*-tolyl sulfone in the ratio 0.35 : 0.20 : 0.45. Flash chromatography of the oil applied in dichloromethane, with ether–light petroleum (b.p. 30–40 °C) (1 : 3, v/v) as the eluent, effected separation between the *Z* isomer, which was obtained as an oil, δ_H(200 MHz, $CDCl_3$) 7.79 (2 H, d, Ar), 7.34 (2 H, d, Ar), 6.30 (1 H, d, *J* 9.4, 3-H), 5.56 (1 H, dt, *J* 9.5, *J'* 7.8, 2-H), 3.96 (2 H, d, *J* 7.7, 1-H), 2.45 (3 H, s, $CH_3C_6H_4$) and 2.14 (3 H, s, SCH_3), and the *E* isomer, which, upon recrystallisation [ether–light petroleum (b.p. 40–60 °C)], was obtained as needles (0.15 g, 25%), m.p. 77–80 °C (lit.,[6] 79–80 °C), δ_H(200 MHz, $CDCl_3$) 7.73 (2 H, d, Ar), 7.35 (2 H, d, Ar), 6.16 (1 H, d, *J* 15.0, 3-H), 5.22 (1 H, dt, *J* 15.1, *J'* 7.6, 2-H), 3.81 (2 H, d, *J* 7.4, 1-H), 2.45 (3 H, s, $CH_3C_6H_4$) and 2.23 (3 H, s, SCH_3).

Rearrangement of (Z)- and (E)-3-*Methylthioallyl* p-*Tolyl Sulfone*.—The *Z* and *E* isomers of the title compound (25 mg, 0.10 mmol) were each dissolved in carbon tetrachloride (5 cm^3) with dibenzoyl peroxide (2.5 mg, 0.01 mmol, 10 mol%) and the solutions heated under reflux at 90 °C for 18 h; after this the solvent was removed under reduced pressure. In each case, the resulting oil was shown by ^1H NMR spectroscopy to be a mixture of the *Z* and *E* isomers of 3-methylthioallyl *p*-tolyl sulfone in the *Z* : *E* ratio 1.0 : 1.0 (starting from the *Z* isomer) and 0.45 : 1.0 (from the *E* isomer).

1-*Deuterio*-1-*methylthioallyl* p-*Tolyl Sulfone*.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 2.8 cm^3, 4.5 mmol) was added by syringe with stirring to diisopropylamine (1.0 cm^3, 7.1 mmol), followed by dry THF (15 cm^3), and the resulting solution was cooled in an acetone–solid CO_2 slush bath. 1-Methylthioprop-1-enyl *p*-tolyl sulfone (0.90 g, 3.7 mmol) dissolved in dry THF (5 cm^3) was added *via* a needle tube over 5 min to the solution which was then stirred for 10 min before being quenched by the addition of [^2H]acetic acid (1.0 cm^3, 1.1 g, 17 mmol). Diethyl ether (60 cm^3) was added to the mix-

ture which was then allowed to warm to room temperature. It was then washed with aq. HCl (50 cm^3), water (2 × 50 cm^3) and brine (50 cm^3), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a yellow solid (0.79 g). Flash chromatography of this, applied in dichloromethane, and using diethyl ether–light petroleum (b.p. 30–40 °C) as the eluent gave the product as a yellow solid (0.43 g, 48% yield); the ^1H NMR spectrum showed increased complexity in the multiplet at δ 5.74–5.92, and a diminution of the intensity of the doublet at δ 4.37 corresponding to 58% deuteriation; δ_D(250 MHz, $CHCl_3$) 4.36 (s, 1-D).

Rearrangement of 1-*Deuterio*-1-*methylthioallyl* p-*Tolyl Sulfone*.—The product from the previous reaction, a 1.4:1.0 mixture of 1-deuterio-1-methylthioallyl *p*-tolyl sulfone and 1-methylthioallyl *p*-tolyl sulfone (0.25 g, 1.0 mmol) and dibenzoyl peroxide (0.025 g, 0.10 mmol, 10 mol%) were dissolved in carbon tetrachloride (29 cm^3) and heated under reflux at 90 °C for 16 h. After cooling to room temperature, the solution was washed with aq. sodium metabisulfite (20 cm^3), aq. HCl (30 cm^3) and water (30 cm^3), dried ($CaCl_2$), filtered and evaporated under reduced pressure to give an oil (0.26 g). ^1H NMR spectroscopy showed that the oil consisted of starting material, and (*Z*)- and (*E*)-3-methylthioallyl *p*-tolyl sulfone in ratio 1.0:0.7:1.5 all of which had deuterium incorporated α to the SMe; the decrease in intensities of the corresponding signals showed the percentage deuteriation of these three isomers to be 55, 58 and 63%, respectively (with an uncertainty in each case of about 6%); δ_D(250 MHz, $CDCl_3$) 6.33 (s, 3-D, *Z* isomer), 6.21 (s, 3-D, *E* isomer) and 4.37 (1-D, starting material); the first two peaks were not fully resolved, but the second was more intense than the first; the ratio of intensities of the first two peaks to the second was 2.7:1.

Treatment of p-*Tolyl* 1-p-*Tolylthioallyl Sulfone* **3** *with* BPO–CCl_4.—*p*-Tolyl 1-*p*-tolylthioallyl sulfone (500 mg, 1.57 mmol) was dissolved in carbon tetrachloride (20 cm^3) and benzoyl peroxide (38 mg, 0.16 mmol, 10 mol%) was added to the solution. This was then heated under reflux with stirring for 24 h, after which further benzoyl peroxide (20 mg) was added to it. The mixture was refluxed for a further 24 h, and allowed to cool, to yield brown crystals, which were insoluble in carbon tetrachloride and in aqueous solvents. These crystals were filtered off and shown by ^1H NMR to be *p*-tolyl 3-*p*-tolylsulfonylprop-1-enyl sulfone **10** (103.3 mg, 19%); δ_H(200 MHz) 7.70 (2 H, d, Ar), 7.63 (2 H, d, Ar), 7.35 (2 H, d, Ar), 7.24 (2 H, d, Ar), 6.75 (1 H, m, 2-H), 6.35 (1 H, d, *J* 15.1, 1-H), 3.92 (2 H, d, *J* 7.8, 3-H), 2.46 (3 H, s, MeC_6H_4) and 2.40 (3 H, s, $CH_3C_6H_4$). The filtrate was washed with aq. NaOH (20 cm^3), aq. sodium metabisulfite (20 cm^3), aq. HCl (20 cm^3) and water (20 cm^3), dried ($CaCl_2$), and evaporated under reduced pressure to yield an oil. Flash column chromatography of this with diethyl ether–light petroleum (b.p. 30–40 °C) (1:4) as the eluent, effected partial separation of the products as five main fractions. Fraction 1 contained two compounds shown by later comparison to be the (*E*)- and (*Z*)-*p*-tolyl 3-*p*-tolylthioprop-1-enyl sulfide **14** and **15**, in the ratio (1:0.54); δ_H(200 MHz) 7.7–6.9 (8 H, m, Ar, both isomers), 6.26 (1 H, d, *J* 9.17, 1-H, *Z* isomer), 6.09 (1 H, d, *J* 14.84, 1-H, *E* isomer), 5.89–5.78 (1 H, m, 2-H), 3.74 (2 H, d, *J* 7.35, 3-H, *Z* isomer), 3.55 (2 H, d, *J* 7.24, 3-H, *E* isomer) and 2.37 and 2.33 (6 H, s, $CH_3C_6H_4$, both isomers). Fraction 2 contained unchanged starting material. Fraction 3 contained *p*-tolyl 3-*p*-tolylthioallyl sulfone **12** and **13** in an *E*:*Z* ratio of 1:2.4; δ_H(200 MHz) 7.82 (2 H, d, Ar, *Z* isomer), 7.73 (2 H, d, Ar, *E* isomer), 7.35 (2 H, d, Ar, *Z* isomer), 7.45–7.0 (6 H, m, Ar, *E* isomer), 7.03 (4 H, s, Ar, *Z* isomer), 6.48 (1 H, d, *J* 9.4, 1-H, *Z* isomer), 6.21 (1 H, d, *J* 15.05, 1-H, *E* isomer), 5.73 (1 H, dt, *J* 9.34, 7.73, 2-H, *Z* isomer), 5.44 (1 H, dt, *J* 15.5, 7.7, 2-H, *E* isomer), 4.08 (2 H, d, *J* 7.81, 3-H, *Z* isomer), 3.73 (2 H, d, *J* 6.98, 3-H, *E* isomer), 2.47 (3 H, s, $CH_3C_6H_4$, *E* isomer), 2.44 (3 H, s, $CH_3C_6H_4$, *Z* isomer), 2.35 (3 H, s, $CH_3C_6H_4$, *E* isomer) and 2.31 (3 H, s, $CH_3C_6H_4$, *Z* isomer). Fraction 4 contained *p*-tolyl 3-*p*-tolylthioallyl sulfone (*E* and *Z* isomers) **12** and **13** and *p*-tolyl 3-*p*-tolylthioprop-1-enyl sulfone **11** (*E* isomer only); δ_H(200 MHz) 7.60 (2 H, d, Ar), 7.35 (2 H, d, Ar), 7.16 (2 H, d, Ar), 6.94 (2 H, d, Ar), 6.88 (1 H, m, 2-H), 6.10 (1 H, d, *J* 14.88, 1-H), 3.51 (2 H, d, *J* 7.27, 3-H), 2.44 (3 H, s, $CH_3C_6H_4$) and 2.26 (3 H, s, $CH_3C_6H_4$) in the ratio 1:2.5:0.9. Crystallisation from EtOH gave *p*-tolyl (*E*)-3-*p*-tolylthioallyl sulfone **12** as crystals (19.3 mg, 3.9%), m.p. 108–109 °C (lit.,[5] 109–110 °C); ^1H NMR data as above. Fraction B contained compounds **12**, **13**, **11** and **10** in the ratio 1:0.45:0.4:0.47.

In a control reaction, the sulfone **3** (30 mg, 0.09 mmol) was dissolved in carbon tetrachloride (10 cm^3), and the mixture was refluxed for 24 h. The solvent was removed under reduced pressure, and the product examined by ^1H NMR spectroscopy. The product was entirely unchanged starting material.

Rearrangement of p-*Tolyl* (E)- *and* (Z)-3-p-*Tolylthioallyl Sulfone*.—*p*-Tolyl (*E*)- and (*Z*)-3-*p*-tolylthioallyl sulfone (130 mg, 0.41 mmol) in an *E*:*Z* ratio of 1:2.4 was dissolved in carbon tetrachloride (15 cm^3) and benzoyl peroxide (10 mg, 0.04 mmol, 10 mol%) was added to the mixture. This was stirred and heated under reflux for 24 h after which benzoyl peroxide (5 mg) was added to it. Stirring and heating was continued for a further 24 h. The solution was washed with aq. NaOH, aq. sodium metabisulfite, aq. HCl and water (all 15 cm^3), dried ($CaCl_2$), and evaporated under reduced pressure. Examination of the ^1H NMR spectrum of the residue showed that the *E*:*Z* ratio had changed to 0.9:1.

Rearrangement of p-*Tolyl* (E)-3-p-*Tolylthioallyl Sulfone* **12**.—*p*-Tolyl (*E*)-3-*p*-tolylthioallyl sulfone (19.3 mg, 0.06 mmol) was dissolved in carbon tetrachloride (5 cm^3), and benzoyl peroxide (1.5, 10 mol%) was added to the solution. The mixture was allowed to reflux for 24 h, after which further benzoyl peroxide (0.80 mg) was added to it. The mixture was refluxed for a further 24 h after which it was evaporated under reduced pressure, and the product examined by ^1H NMR spectroscopy. The product consisted of the *E* and *Z* isomers **12** and **13** in the ratio 1:0.64.

1,3-*Bis*(p-*tolylthio*)*propane*-2-*yl Toluene*-p-*sulfonate*.—Potassium hydroxide (9.21 g, 0.16 mol) in ethanol (140 cm^3) was added to *p*-thiocresol (20.4 g, 0.16 mol) and the solution was cooled in an ice-bath. Epichlorohydrin (7.6 g, 0.08 mol) was slowly added to the stirred solution after which the mixture was stirred at 0–5 °C for 30 min and then at 18 °C for 2 h. After this the mixture was diluted with water (120 cm^3) and extracted with chloroform (3 × 30 cm^3). The combined extracts were washed with aq. NaOH and water (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to yield 1,3-bis(*p*-tolylthio)propan-2-ol as an oil (19.32 g); δ_H(200 MHz) 7.26 (4 H, d, Ar), 7.09 (4 H, d, Ar), 3.77 (1 H, m, 2-H), 3.15 (dd, 2H, *J* 4.9, 13.7, 1-H and 3-H), 2.99 (dd, 2 H, *J* 7.2, 13.7, 1-H and 3-H) and 2.33 (6 H, s, $CH_3C_6H_4$).

The above product (6 g, 19.7 mmol) was dissolved in pyridine (50 cm^3) and the solution cooled in an ice-bath. Purified toluene-*p*-sulfonyl chloride (5.6 g, 29.6 mmol) was added to the cooled, stirred solution, which was then removed from the ice-bath. The mixture was stirred for 1 h and then left for 16 h after which it was treated with water (2 cm^3) and set aside for 15 min. An excess of water was then added to the mixture (100 cm^3) after which it was extracted with ether (3 × 25 cm^3). The combined extracts were washed with aq. HCl, aq. NaOH and water (all 25 cm^3) and then dried ($MgSO_4$) and evaporated

under reduced pressure. Crystallisation of the residue from ether–light petroleum (b.p. 30–40 °C) yielded the *title compound* (2.2 g, 24%), m.p. 75 °C (Found: C, 62.85; H, 5.7. $C_{24}H_{26}O_3S_3$ requires C; 63.15, H; 5.7%); δ_H(200 MHz) 7.57 (2 H, d, Ar), 7.16 (2 H, d, Ar), 7.08 (4 H, br t, Ar), 4.48 (1 H, qn, *J* 8.0, 2-H), 3.24 (4 H, d, 1-H and 3-H), 2.43 (3 H, s, MeC_6H_4) and 2.35 (6 H, s, $CH_3C_6H_4$).

p-*Tolyl* 3-p-*Tolylthioprop*-1-*enyl Sulfide*.—DBU (0.5 cm^3, 3.3 mmol) was added to a solution of 1,3-bis-(*p*-tolylthio)propan-2-yl tosylate (500 mg, 1.1 mmol in toluene (40 cm^3), and the mixture was stirred and refluxed for 5 h. It was then cooled and most of the toluene was removed under reduced pressure. Chloroform (20 cm^3) was added to the residue and the mixture was washed with aq. HCl and water (10 cm^3 each), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dissolved in the minimum amount of chloroform–light petroleum (b.p. 30–40 °C) and passed through a silica plug. The fractions were bulked, and the solvent removed under reduced pressure. Flash column chromatography with ether–light petroleum (b.p. 40–40 °C) 1:9 gave (*E*)- and (*Z*)-*p*-tolyl 3-*p*-tolylthioprop-1-enyl sulfide (23.4 mg, 7%) in an *E*:*Z* ratio of 1:0.65; δ_H(200 MHz) 7.4–6.9 (4 H, m, Ar, both isomers), 6.26 (1 H, d, *J* 9.17, 1-H, *Z* isomer), 6.09 (1 H, d, *J* 14.84, 1-H, *E* isomer), 5.9–5.7 (1 H, m, 2-H, both isomers), 3.74 (2 H, d, *J* 7.35, 3-H, *Z* isomer), 3.55 (2 H, d, *J* 7.2, 3-H, *E* isomer) and 2.37–2.33 (6 H, m, $CH_3C_6H_4$, both isomers).

1-*Methylsulfonyl*-1-p-*tolylsulfonylprop*-2-*ene* **16**.—A solution of potassium hydrogen persulfate, OXONE® (47%; 6.0 g, 18.6 mmol) in water (30 cm^3) was added dropwise over 5 min with cooling (ice-bath) to a stirred solution of 1-methylthioallyl *p*-tolyl sulfone (1.5 g, 6.2 mmol) in methanol (30 cm^3). The resulting white slurry was stirred for 8 h at 18 °C and then diluted with water (70 cm^3) and extracted with chloroform (3 × 50 cm^3). The combined extracts were washed with water (100 cm^3) and brine (100 cm^3), dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Recrystallisation [chloroform–light petroleum (b.p. 40–60 °C)] of the residue gave the *title compound* as crystals (1.22 g, 72%), m.p. 118–121 °C [from ethyl acetate–light petroleum (b.p. 40–60 °C)] (Found: C, 48.45; H, 5.3; S, 22.6. $C_{11}H_{14}O_4S_2$ requires: C, 48.15; H, 5.15; S, 23.35%); δ_H(500 MHz, $CDCl_3$) 7.81 (2 H, d, ArH), 7.38 (2 H, d, ArH), 5.84 (1 H, ddd, *J* 10.0, *J'* 10.0, *J''* 16.8, 2-H), 5.73 (1 H, d, *J* 10.1, 3-H'), 5.59 (1 H, d, *J* 16.8, 3-H''), 4.78 (1 H, d, *J* 9.8, 1-H), 3.31 (3 H, s, SO_2Me) and 2.48 (3 H, s, MeC_6H_4).

Rearrangement of 1-*Methylsulfonyl*-1-p-*tolylsulfonylprop*-2-*ene*.—Compound **16** (1.4 g, 5.10 mmol) and dibenzoyl peroxide (0.124 g, 0.51 mmol) were dissolved in chloroform (50 cm^3; stored over $CaCl_2$ in the dark and filtered through active alumina before use to remove ethanol), and heated under reflux at 80 °C for 18 h. Solvent was removed *in vacuo* from the mixture to give an oil; flash chromatography of this, the material being applied in dichloromethane, and subjected to graded elution with ether–light petroleum (b.p. 30–40 °C) mixtures gave: starting material isomerising to the vinyl isomers on the column; (*E*)-1,3-di(*p*-tolylsulfonyl)propene **17**; a 1.0:1.0 mixture of (*E*)-1-methylsulfonyl 3-*p*-tolylsulfonylprop-1-ene **20** and (*E*)-3-methylsulfonyl-1-*p*-tolylsulfonylprop-1-ene **19**; and (*E*)-1,3-di(methylsulfonyl)propene **18**. ^1H NMR spectroscopy of the crude product showed it to contain **16**, **17**, **19**, **20** and **18** in ratio 0.4:1.0:0.9:0.9:0.7.

(*E*)-1,3-Di(*p*-tolylsulfonyl)propene **17**, on recrystallisation from chloroform–light petroleum (b.p. 40–60 °C), gave crystals (0.27 g, 15%), m.p. 151–153 °C (lit.,[12] 146–147 °C); δ_H(500 MHz, $CDCl_3$) 7.71 (2 H, d, ArH), 7.64 (2 H, d, ArH), 7.37 (2 H, d, ArH), 7.26 (2 H, d, ArH), 6.75 (1 H, dt, *J* 7.7, *J'* 15.1, 2-H), 6.35 (1 H, d, *J* 15.1, 1-H), 3.91 (2 H, d, *J* 7.8, 3-H), 2.48 (3 H, s, MeC_6H_4) and 2.43 (3 H, s, MeC_6H_4). The 1.0:1.0 mixture of (*E*)-1-methylsulfonyl-3-*p*-tolylsulfonylprop-1-ene **20** and (*E*)-3-methylsulfonyl-1-*p*-tolylsulfonylprop-1-ene **19** was recrystallised [chloroform–light petroleum (b.p. 40–60 °C)] to give pale brown crystals (0.40 g, 29%) of the two isomers in the same ratio (Found: C, 48.35; H, 4.8. $C_{11}H_{14}O_4S_2$ requires C, 48.15; H, 5.15%); δ_H(500 MHz, $CDCl_3$) **19** 7.79 (2 H, d, ArH), 7.38 (2 H, d, ArH), 6.95 (1 H, dt, *J* 7.6, *J'* 15.2, 2-H), 6.72 (1 H, d, *J* 15.2, 1-H), 3.87 (2 H, d, *J* 7.7, 3-H), 2.90 (3 H, s, SO_2Me) and 2.46 (3 H, s, MeC_6H_4); **20** 7.77 (2 H, d, ArH), 7.40 (2 H, d, ArH), 6.78 (1 H, dt, *J* 7.6, *J'* 15.2, 2-H), 6.52 (1 H, d, *J* 15.1, 1-H), 3.97 (2 H, d, *J* 7.6, 3-H), 2.91 (3 H, s, SO_2Me_3) and 2.48 (3 H, s, MeC_6H_4). The NMR assignments to **19** and **20** are based on oxidation of (*E*)-3-methylthioallyl *p*-tolyl sulfone **8** to a mixture of **19** and **20** in which the latter predominated (see below).

(E)-1,3-*Dimethylsulfonylpropene* **18**, on recrystallisation [chloroform–light petroleum (b.p. 40–60 °C)], gave needles (0.025 g, 2.5%), m.p. 134–135 °C [chloroform–light petroleum (b.p. 40–60 °C)] (Found: C, 30.3; H, 5.1. $C_5H_{10}O_4S_2$ requires C, 30.3; H, 5.1%); δ_H(500 MHz, [$^2H_6$]-DMSO) 7.09 (1 H, d, 1-H), 6.67 (1 H, dt, *J* 7.6, *J'* 15.1, 2-H), 4.25 (2 H, d, *J* 7.6, 3-H), 3.09 (3 H, s, SO_2Me) and 3.04 (3 H, s, SO_2Me).

In a control experiment a 1:1 mixture of **19** and **20** (50 mg, 0.18 mmol) and dibenzoyl peroxide (4.4 mg, 0.018 mmol) in deuteriochloroform (2 cm^3) was heated under reflux at 80 °C whilst its ^1H NMR spectrum was recorded at intervals. After 72 h, the ^1H NMR spectrum revealed that only unchanged starting materials were present in the same ratio.

Oxidation of (E)-3-*Methylthioallyl* p-*Tolyl Sulfone*.—A solution of potassium hydrogen persulfate, OXONE® (47%; 68 mg, 0.21 mmol) in water (2 cm^3) was added over 1 min with cooling (ice-bath) to a stirred solution of (*E*)-3-methylthioallyl *p*-tolyl sulfone **8** (17 mg, 0.07 mmol) in methanol (2 cm^3). The resulting white slurry was stirred at room temperature for 5 h and then diluted with water (5 cm^3) and extracted with chloroform (3 × 5 cm^3). The combined extracts were washed with water (10 cm^3) and brine (10 cm^3), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a white solid (22 mg) consisting of (*E*)-1-methylsulfonyl-3-*p*-tolylsulfonylprop-1-ene **20** and (*E*)-3-methylsulfonyl-1-*p*-tolylsulfonylprop-1-ene **19** in ratio 2.6:1.0; ^1H NMR data as above.

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