1,3-Rearrangements of Some Allylic Sulphones

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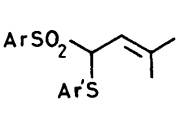
The 1,3-rearrangement of a number of acyclic and cyclic allylic *p*-tolyl sulphones has been found to occur on treatment (*a*) with benzoyl peroxide (BPO) in CCl_4 under reflux or (*b*) with sodium toluene-*p*-sulphinate in aqueous acetic acid at 110 °C. Rearrangement is only successful in cases where the product sulphone is thermodynamically more stable than the starting material, *e.g.* prenyl† sulphone (**10**) is obtained from dimethylallyl sulphone (**9**). A radical chain addition–elimination mechanism involving arenesulphonyl radicals is proposed.

More heavily substituted cyclic allylic sulphones such as 1-methylcyclohex-2-enyl *p*-tolyl sulphone (**21**; R = Me) rearranged only sluggishly under the BPO–CCl_4 conditions but underwent smooth isomerisation to (**22**; R = Me) on being heated in AcOH–water (3:2) at 110 °C. Evidence is presented in favour of an ion-pair dissociation–recombination mechanism in these cases.

Prior to 1980 there were a number of isolated examples in the literature of 1,3-rearrangements of allylic sulphones. Mislow *et al.*[1] reported that α-methylallyl *p*-tolyl sulphone rearranged partially to crotyl sulphone when allowed to stand for several days. Bordwell and Pagani[2] found that rearrangement of the substituted sulphone (**1**) to its isomer (**2**) occurred on methanolysis at 50 °C or on treatment with silica gel or alumina in benzene. A Hoffmann–La Roche group[3] described isomerisation of the sulphone (**3**) to (**4**) on treatment with acetic acid at room temperature. The much cited paper of Cope *et al.*[4] has also been quoted[5] as an early precedent, but in fact Cope never made such a claim and there are a number of possible interpretations of his experimental data.

Since 1980, and roughly contemparaneous with our investigations,[6] a number of relevant publications have appeared. Thermal 1,3-rearrangement of the deuterium labelled sulphone (**5**) in nitrobenzene at 150 °C has been studied and a



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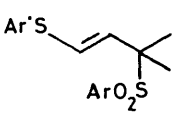

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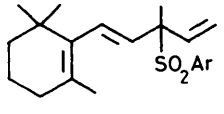

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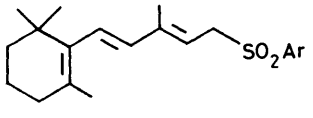

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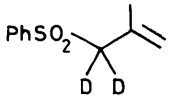
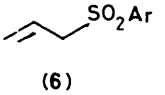


(5)

dissociation–recombination mechanism involving allylic and benzenesulphonyl radicals was suggested.[7] A number of substituted acyclic allylic sulphones has been found to undergo allylic or *E,Z* rearrangement, in competition with epoxidation, when treated with *m*-chloroperbenzoic acid in CH_2Cl_2–water containing $NaHCO_3$.[8] The latter isomerisations appear to be closely related to our studies and we shall refer to them again later. Also closely related to our work is a report by Julia *et al.*[9] on the rearrangement of 1,1-dimethylallyl *p*-tolyl sulphone to prenyl sulphone and an analogous rearrangement of linalyl sulphone catalysed by toluene-*p*-sulphinic acid. It has also been found that rearrangement of allylic sulphones can be catalysed by $Pd(Ph_3P)_4$.[10] Here Π-allyl complexes are implicated[11] and this work will not be discussed further as it is apparently not mechanistically related to our systems. A very recent publication by Ogura *et al.*[12] gives further examples of rearrangements of substrates of the type investigated earlier by Bordwell (see above) carried out under solvolytic conditions and initiated either thermally or photochemically. In another recent paper, Little *et al.*[13] have described the gas-phase thermal rearrangement of deuterium-labelled allyl s-butyl sulphone; analogies are drawn with the work of Baechler[7] and some possible mechanisms are ruled out but no definitive mechanistic conclusions are reached.

Results and Discussion

When we began our investigations on the 1,3-rearrangement of allylic sulphones, the original motivation was synthetic. It was envisaged that, for example, allyl *p*-tolyl sulphone (**6**) (unless



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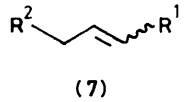


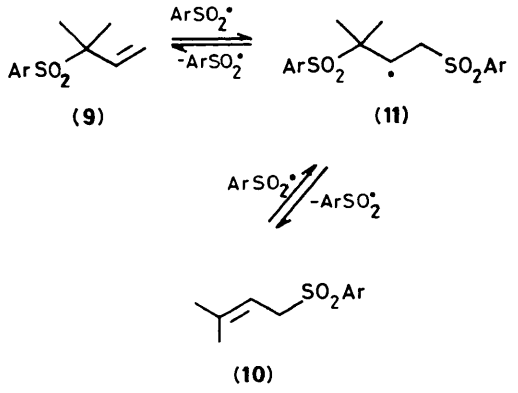
(7)

(8)

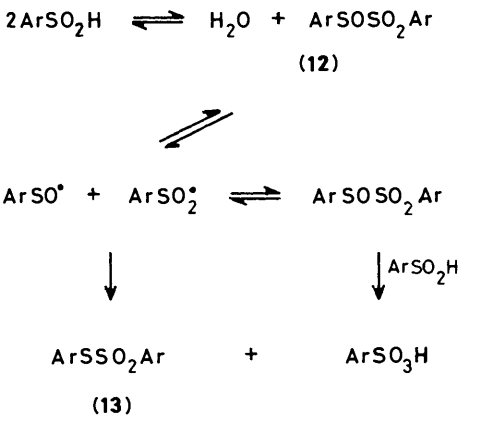
otherwise stated, Ar = *p*-C_6H_4Me) might be subjected successively to α-alkylation (R′), 1,3-rearrangement, further α-alkylation (R^2), and regioselective replacement of $ArSO_2$ by H to give an alkene (**7**). In this way the sulphone (**6**) would be being used as the synthetic equivalent of the allyl dianion (**8**). With additional alkylation steps the tri- and tetra-anion would be simulated.

Dimethylallyl *p*-tolyl sulphone (**9**) was used as a convenient substrate for our initial experiments on the 1,3-rearrangement as it has a simple ^1H n.m.r. spectrum, easily distinguished from that of the isomer (**10**). It soon transpired that radical initiators promoted the desired reaction and we established standard conditions [5 mol % dibenzoyl peroxide (BPO); 0.1M-solution in CCl_4; 18 h reflux] under which rearrangement went to completion. Azoisobutyronitrile (AIBN) was less effective as an initiator. As expected for a radical chain reaction, rearrangement in the absence of initiators was capricious, sometimes occurring and sometimes not. However rearrangement was consistently inhibited in control experiments in the presence of hydroquinone. We consider that under the standard BPO conditions rearrangement involves, as chain propagating steps, the addition and elimination of arenesulphonyl radicals with radical (**11**) as the key intermediate (Scheme 1). Presumably the

† Prenyl = $Me_2C{=}CHCH_2$.



Scheme 1.



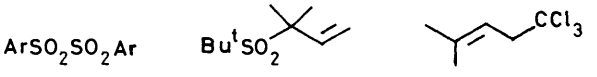
Scheme 2.

initiation step comprises the addition of phenyl or benzoyloxyl radicals to (**9**) leading, *via* elimination, to arenesulphonyl radicals thereby establishing the chain. The proposed mechanism is closely related to that advanced by Kocienski[8] for rearrangement accompanying epoxidation of some methyl substituted allyl *p*-tolyl sulphones but with a different initiating step. It is also akin to one of the mechanisms accepted for 1,3-rearrangement of allylic sulphides[14] which are much more labile. We do not favour a radical dissociation–recombination mechanism as proposed for the rearrangement of the sulphone (**5**) at higher temperatures[7] since it would be less easy to accommodate the initiation/inhibition evidence on this basis.

There are a number of precedents for radical processes of the type suggested. Sulphonyl radicals are well authenticated intermediates[15] and they have previously been implicated in addition–elimination mechanisms to explain rearrangements of *N*-vinylsulphonamides[16] and enol sulphonates.[17] Radical substitution reactions involving γ-attack on an allylic sulphone are known[18] and sulphonyl radical elimination from β-sulphonyl radicals has been studied in a variety of situations.[19] It seems likely that Mislow's observation of rearrangement of an allylic sulphone[1] was an early example of the radical chain isomerisation.

We have also found, thereby corroborating the observations of Julia,[9] that conversion of dimethylallyl-(**9**) into the prenyl sulphone (**10**) was promoted by toluene-*p*-sulphinic acid. This was most conveniently carried out using sodium toluene-*p*-sulphinate in aqueous acetic acid. Toluene-*p*-sulphinic acid has pK_a *ca.* 1.29 and it was established by $CHCl_3$ extraction that the free acid was present in the solution. Conditions under which rearrangement was complete were: $ArSO_2Na$ (7 mol equiv.); AcOH–water (3:2); 8 h at 110 °C. Rerrangement was also complete with only one equivalent of sulphinate but we generally used the larger excess as standard since it was more effective for subsequent, more sluggish isomerisations. We originally envisaged that the sulphinate-promoted rearrangement involves some kind of S_N2^1 or $S_{RN}1$ process,[6] but we now believe that the sulphinic acid behaves as an alternative source of $ArSO_2^{\bullet}$ radicals thereby establishing the same propagating steps involving (**11**) proposed above for the BPO–CCl_4 conditions. Evidence in favour of this view is that sodium toluene-*p*-sulphinate in the absence of acid is not an effective catalyst and under limiting conditions for rearrangement [$ArSO_2Na$ (0.1 mol equiv.); AcOH–water; 100 °C] inhibition by hydroquinone was found. Kice[20] has shown that one step in the disproportionation of arenesulphinic acids to thiol-sulphonate (**13**) (always a by-product in our sulphinate induced reactions) and sulphonic acid is the homolytic dissociation of the arenesulphinyl aryl sulphone (**12**), and this step could be the source of arenesulphonyl radicals (Scheme 2). In agreement we find[21] the sulphinyl sulphone (**12**) to be effective at promoting the rearrangement of (**9**) to (**10**) (in CCl_4). Unfortunately the relative instability of (**12**) precludes its use as a convenient storable initiator for the isomerisation. Other formally possible sources of $ArSO_2^{\bullet}$, such as the thiolsulphonate (**13**) and bis-sulphone (**14**) fail to catalyse the rearrangement of (**9**) to (**10**).[21] This is in line with the known lesser ease of homolytic dissociation of these compounds compared to (**12**).[20,22] Further evidence in favour of the radical chain mechanism for the sulphinate-induced rearrangement is provided from studies on the cyclic allylic sulphones to be discussed later.

Dimethylallyl t-butyl sulphone (**15**) was much more stable to BPO–CCl_4 than the corresponding aryl sulphone (**9**), being virtually unchanged under the standard conditions. On prolonged treatment, 5,5,5-trichloro-2-methylpent-2-ene (**16**) and

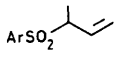
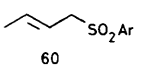
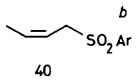
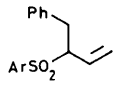
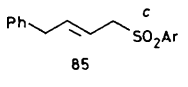
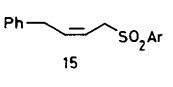
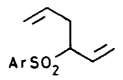
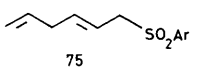
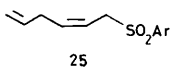
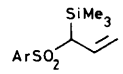
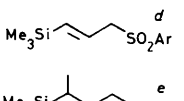
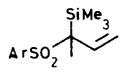
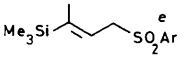


t-butyl chloride were obtained; with $BrCCl_3$–CCl_4–BPO more rapid formation of (**16**) and t-butyl bromide was observed.[23] Apparently radical addition–elimination[18] (S_H2^1) leads to $ButSO_2^{\bullet}$ radicals which are relatively unstable with respect to sulphur dioxide and t-butyl radicals. The t-Bu$^{\bullet}$ radical can then maintain a chain process leading, *via* halogen abstraction from CCl_4 (or $BrCCl_3$), to attack of $Cl_3C^{\bullet}$ on the sulphone (**15**). These observations provide circumstantial evidence in favour of the radical chain mechanism for 1,3-rearrangement of allylic sulphones.

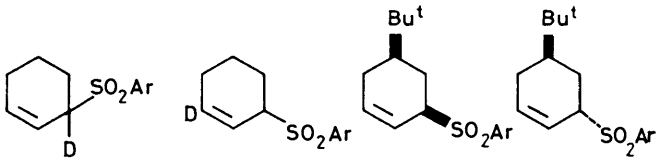
A number of 1-substituted allyl sulphones underwent 1,3-rearrangement under the standard BPO–CCl_4 conditions and the results are summarised in Table 1. In general the more substituted double bond (more stable) isomer predominated and *E*/*Z* isomeric mixtures were obtained, except for the two trimethylsilyl substituted cases where one isomer, considered to be *E* on steric grounds, was formed. For entries 1 and 2 (Table 1) isolation of one of the diastereoisomeric products followed by resubmission to the BPO–CCl_4 conditions led to re-equilibration. The results are compatible with the $ArSO_2^{\bullet}$ addition–elimination mechanism already discussed leading to interconversion between the various possible 1,3-rearranged isomers. Application of the sulphinate-induced standard conditions to the sulphones listed in Table 1 was also explored. This was effective in the case of entries 1, 2, and 3 but not for 4 and 5 since in these cases protodesilylation was the dominant process.

We next investigated 1,3-rearrangements in six-membered alicyclic systems using [1-^{2}H]cyclohex-2-enyl *p*-tolyl sulphone

Table 1. 1,3-Rearrangement of 1-substituted allyl sulphones in CCl_4 catalysed by BPO

Entry	Substrate	Yield (%)	Products[a] (%)	
1		92	 60	 40
2		84	 85	 15
3		80	 75	 25
4				
5				

[a] Analysis of crude product mixture by n.m.r. spectroscopy. [b] *Z*-Sulphone re-equilibrated with *E*-sulphone under reaction conditions. [c] *E*-Sulphone re-equilibrated with *Z*-sulphone under reaction conditions. [d] Obtained as 6:4 mixture with starting material. [e] Obtained as 9:1 mixture with starting material.



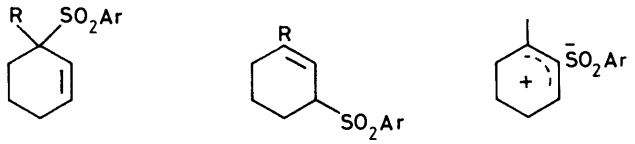
(17) (18) (19) (20)

(**17**).[24] Equilibration with isomer (**18**) was achieved under either the BPO–CCl_4 or sulphinate-induced conditions, inhibition by hydroquinone was demonstrated, and it was shown that (**17**) did not rearrange on heating in AcOH–water (3:2) alone. With the conformationally-biased 5-t-butyl substituted sulphones (**19**) and (**20**), treatment with sodium toluene-*p*-sulphinate in AcOH–water (3:2) at 110 °C gave the equilibrium mixture[24] (**19**):(**20**) of 6:4. The use of the [1-^{2}H]-labelled sulphones (**19**) and (**20**) showed that epimerisation was accompanied by 1,3-rearrangement and it was confirmed that neither epimerisation nor ^{2}H scrambling occurred on prolonged heating in AcOH–water in the absence of sodium sulphinate. Further, sodium bromide in AcOH–water had no effect, indicating that the role of the sodium sulphinate is not merely a salt effect. Finally, by finding conditions under which only partial rearrangement occurred in the presence of sodium toluene-*p*-sulphinate, it was shown that, within experimental error, the rates of epimerisation and ^{2}H scrambling were the same. This result is as expected for a mechanism involving addition–elimination of $ArSO_2^{\bullet}$ and makes unlikely any purely S_N2,S_N2' or concerted cyclic process.*

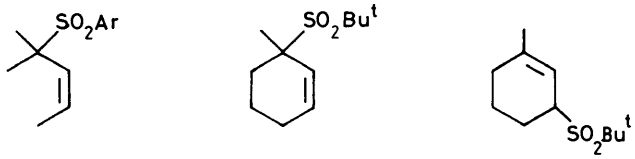
Attempts to apply the BPO–CCl_4 conditions to the 1,3-rearrangement of 1-alkyl substituted cyclohex-2-enyl sulphones were less successful. Thus the 1-methyl sulphone (**21**; R = Me) only underwent partial conversion (25%) to the isomer (**22**; R = Me) under standard conditions (18 h reflux). Even after 54 h, with addition of fresh BPO, the extent of isomerisation was only 75% and formation of by-products was apparent. Similar results were obtained with other 1-alkyl substituents. We consider that the radical addition–elimination mechanism is disfavoured in these cases. Axial addition of $ArSO_2^{\bullet}$ at C-3 would necessarily lead to unfavourable 1,3-diaxial sulphonyl–sulphonyl or sulphonyl–methyl interactions in the intermediate radical.

Conversion of the methylated sulphone (**21**; R = Me) into its isomer (**22**; R = Me) did however occur (88% isolated yield) on heating in AcOH–water (3:2) at 100 °C for 8 h in the absence of any additives. Control experiments showed that this isomerisation was not inhibited by hydroquinone, that it did not occur efficiently on heating in glacial acetic acid, but that other solvent mixtures of relatively high ionising power *e.g.* 50% aqueous formamide were effective. The aqueous acetic acid conditions were adopted as standard and it was shown that 1-ethyl- and 1-benzyl-cyclohex-2-enyl *p*-tolyl sulphones were also converted to their 1,3-rearranged isomers in this way. As already mentioned, the labelled sulphone (**17**) was not isomerised under these conditions and this was also the case for the t-butyl sulphone (**15**) and the monoalkylated sulphones (entries 1,2, and 3) in Table 1. The dimethylallyl sulphone (**9**) did on occasion slowly isomerise to prenyl sulphone on being heated in aqueous acetic acid but the reaction was very sensitive to the purity of the acetic acid and could be inhibited by hydroquinone.

It is our view that in aqueous acetic acid the 1-alkylcyclohex-2-enyl sulphones rearrange by a dissociation–recombination mechanism involving an ion-pair *e.g.* (**23**). The ion-pair is presumed to be fairly 'intimate' since solvolysis products are not found, however, acetolysis of the *p*-tolyl sulphone (**21**; R = Me, Ar = *p*-$MeC_6H_4SO_2$) in the presence of sodium benzenesulphinate gave some phenyl sulphone (**22**; R = Me, Ar = Ph). This observation is consistent with the ion-pair mechanism but it has to be interpreted with caution in view of our earlier postulation of sulphinate-induced radical processes.



(**21**) (**22**) (**23**)



(**24**) (**25**) (**26**)

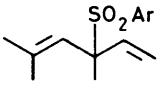
Apparently there are special features about the alkyl substituted cyclohexenyl system favouring the ion-pair since the acyclic analogue (**24**)[24] which could also lead to a 'secondary–tertiary' allylic carbonium ion, does not rearrange under the above aqueous acetic acid conditions. Presumably unfavourable steric interactions are present in the acyclic system which disfavour attainment of the required transition state geometry leading to the planar allylic cation.

Further evidence supporting the ion-pair mechanism for the substituted cyclohexenyl sulphones emerged from an investigation of 1-methylcyclohex-2-enyl t-butyl sulphone (**25**). The sulphone (**25**) was converted to isomer (**26**) under even milder

* We have also found that sodium nitrite (1 mol equiv.) in AcOH–water (3:2) at 100 °C (8 h) catalyses the 1,3-rearrangement of allylic sulphones such as (**9**), entries 1—3 in Table 1, and (**17**) and thereby provides a convenient alternative preparative procedure.[25] No mechanistic investigations on this variant have been carried out but we assume that it is another way of initiating the radical chain.

solvolytic conditions than those required for (**21**) ⟶ (**22**). Thus 70% isomerisation occurred after 8 h in water–AcOH (3:2) at room temperature and could be effected in water–THF (1:1) containing LiI under reflux. Under the latter conditions the corresponding aryl sulphone (**21**; R = Me) was unaffected. The contrast between sulphones (**9**) and (**15**) on the one hand, where the aryl sulphone (**9**) undergoes cleaner and much more rapid rearrangement under radical conditions, and sulphones (**21**; R = Me) and (**25**) on the other, where the t-butyl sulphone (**25**) rearranges more rapidly under ionising conditions is striking. It is difficult to see how this could be explained other than by two different mechanisms. Why the t-butyl sulphone (**25**) is more reactive than (**21**; R = Me) towards dissociation–recombination *via* an ion pair is a matter for speculation. One possibility is that it is a ground state effect whereby the greater steric demands of the t-butyl sulphonyl group compared to the arenesulphonyl group lead to steric acceleration of ionisation.

As already mentioned, Bordwell[2] and Ogura[12] have described substituted acyclic allylic sulphones where an additional cation stabilising substituent (thiophenyl) can facilitate an ion-pair mechanism for 1,3-rearrangement. We consider our substituted cyclohexenyl sulphones to be further examples and we have also found that a second double bond can provide the extra stabilising influence needed to promote the ionisation mechanism. Thus the bis-allylic sulphone (**27**) is



(**27**)

(**28**)

converted to the dienyl sulphone (**28**) on heating in aqueous acetic acid.[26] This example provides a simpler model for the isomerisation (**3**) ⟶ (**4**) mentioned in the introduction,[3] and by analogy supports an ionisation–recombination mechanism in the latter instance.

Experimental

^{1}H N.m.r. spectra were recorded on Perkin-Elmer R24 (60 MHz) or Bruker WH300 (300 MHz) instruments using Me_4Si as an internal standard except for Me_3Si-containing compounds when $CHCl_3$ was used. ^{13}C N.m.r. spectra were obtained from $CDCl_3$ solutions on Bruker WH90 (22.63 MHz) or WH300 instruments (75.43 MHz) using $CDCl_3$ (δ_C 77.00) as an internal standard. ^{2}H N.m.r. spectra were obtained for $CDCl_3$ solutions on a Bruker WH300 instrument (40.07 MHz) using $CDCl_3$ as an internal standard.

Rearrangement of 1,1-*Dimethylallyl* p-*Tolyl Sulphone Using* BPO–CCl_4.—The sulphone[24] as a solution (0.1M) in carbon tetrachloride containing a weighed amount of dibenzoyl peroxide was heated under reflux. At various intervals of time a sample was removed and analysed by ^{1}H n.m.r. spectroscopy (60 MHz). The concentrations of the starting material [δ_H 1.43 (s, Me_2C) and 6.04 (dd, =CH)] and the product [δ_H 1.33 (s, Me), 1.72 (s, Me) and 3.77 (d, CH_2)] were evaluated by integration of the n.m.r. spectrum. Results are given in Table 2.

In a preparative experiment [BPO (5 mol %), CCl_4, reflux (18 h)] the product was isolated and crystallised from ether–light petroleum to give 3-methylbut-2-enyl *p*-tolyl sulphone,[27] m.p. 81 °C (lit.,[27] 81 °C), δ_H 1.33 (3 H, s, =CMe), 1.72 (3 H, s, =CMe), 2.45 (3 H, s, MeAr), 3.77 (2 H, d, *J* 8 Hz, 1-H_2), 5.18 (1 H, br t, 2-H), 7.33 (2 H, d, ArH), and 7.74 (2 H, d, ArH); δ_C 144.46 (s), 142.68 (s), 135.83 (s), 129.57 (d), 128.38 (d), 110.53 (d), 56.15 (t), 25.78 (q), 21.58 (q), and 17.75 (q).

Table 2. Rearrangement of the dimethylallyl sulphone (**9**) to the prenyl sulphone (**10**) using BPO–CCl_4

	(**9**):(**10**) Ratio at stated [BPO]		
t(h)	1 mol %	2 mol %	5 mol %
1	96:4	94:6	58:42
2	85:15	65:35	41:59
4	50:50	28:72	20:80
8	20:80	21:79	—
24	10:90	5:95	0:100

Rearrangement of Allylic Sulphones in Carbon Tetrachloride in the Presence of Dibenzoyl Peroxide: Preparative Procedure.—The sulphone (5 mmol) and dibenzoyl peroxide (5 mol %) were dissolved in carbon tetrachloride (50 ml) and refluxed for 18 h under an inert nitrogen atmosphere. The reaction mixture was set aside to cool and washed with dilute aqueous sodium hydroxide (50 ml), aqueous sodium hydrogen sulphite (5 ml), dilute hydrochloric acid (50 ml), and water (50 ml), and dried ($CaCl_2$). The solution was evaporated and the residual oil was subjected to column chromatography on silica.

(*a*) *Rearrangement of but-3-en-2-yl* p-*tolyl sulphone.* The sulphone was treated in the manner described above and afforded an oil (92%). The oil was judged to be a 60:40 mixture of *E* and *Z* isomers of but-2-enyl *p*-tolyl sulphone. *E*-Isomer:[28] δ_H 1.68 (3 H, d, =CMe), 2.45 (3 H, s, ArMe), 3.71 (2 H, d, *J* 8 Hz, CH_2SO_2), 5.1—6.0 (2 H, m, =CH), 7.34 (2 H, d, ArH), and 7.78 (2 H, d, ArH); *Z*-isomer:[28] δ_H 1.37 (3 H, d, =CMe), 2.45 (3 H, s, ArMe), 3.84 (2 H, d, *J* 8 Hz, CH_2SO_2), 5.1—6.0 (2 H, m, =CH), 7.34 (2 H, d, ArH), and 7.76 (2 H, d, ArH).

(*b*) *Rearrangement of hexa-1,5-dien-3-yl* p-*tolyl sulphone.* Rearrangement of this sulphone under the above reaction conditions led to an *E,Z* mixture of hexa-2,5-dienyl *p*-tolyl sulphones in the ratio 3:1 (80%). *E*-Isomer: δ_H 2.45 (3 H, s, ArMe), 2.75 (2 H, br t, *J* 6.5 Hz, CH_2), 3.75 (2 H, d, *J* 7 Hz, CH_2SO_2), 4.9—5.1 and 5.4—5.9 (5 H, m, =CH), 7.33 (2 H, d, ArH), and 7.73 (2 H, d, ArH); *Z*-isomer: δ_H 2.45 (3 H, s, ArMe), 2.50 (2 H, br t, *J* 6.5 Hz, CH_2), 3.87 (2 H, d, *J* 7 Hz, CH_2SO_2), 4.9—5.1 and 5.4—5.9 (5 H, m, =CH), 7.33 (2 H, d, ArH), and 7.76 (2 H, d, ArH).

(*c*) *Rearrangement of* 1-*phenylbut-3-en-2-yl* p-*tolyl sulphone.* Rearrangement led to an *E,Z* mixture of 4-phenylbut-2-enyl *p*-tolyl sulphone in the ratio 6:1 (84%) *E*-Isomer: δ_H 2.42 (3 H, s, ArMe), 3.32 (2 H, br d, *J* 6.5, 1 Hz, CH_2Ph), 3.76 (2 H, dd, *J* 7.5, 1.0 Hz, CH_2SO_2), 5.49 (1 H, ddt, *J* 15.5, 7.5, 1 Hz, =CH), 5.64 (1 H, ddt, *J* 15.5, 6.5, 1 Hz, =CH), and 6.95—7.35, and 7.6—7.75 (9 H, m, ArH); *Z* isomer: δ_H 2.42 (3 H, s, ArMe), 3.08 (2 H, br d, *J* 6.5 Hz, CH_2Ph), 3.95 (2 H, br d, *J* 7 Hz, CH_2SO_2), 5.5—5.8 and 5.85—5.97 (2 H, m, =CH), and 6.90—7.40 and 7.7—7.78 (9 H, m, ArH). The major isomer was separated by crystallisation from ether–light petroleum, (*E*)-4-*phenylbut-2-enyl* p-*tolyl sulphone* was obtained as white feathery needles (24%) and had m.p. 61—62 °C (Found: C, 71.2; H, 6.25; S, 10.95. $C_{17}H_{18}O_2S$ requires C, 71.3; H, 6.35; S, 11.2%); δ_C 144.51 (s), 139.69 (d), 138.91 (s), 135.26 (s), 129.60 (d), 128.46 (d), 126.27 (d), 117.71 (d), 60.02 (t), 38.84 (t), and 21.59 (q).

(*d*) *Rearrangement of* 1-*Trimethylsilylprop-2-enyl* p-*tolyl sulphone.* The above silyl sulphone was treated with three 5 mol%-batches of dibenzoyl peroxide at *t* = 0, 18, and 32 h and the reactions were worked up as described in the above general procedure to give a mixture (2:3) of starting material and (*E*)-3-trimethylsilylprop-2-enyl *p*-tolyl sulphone (as shown by n.m.r. spectroscopy). The latter sulphone was purified by refluxing the mixture in 10% aqueous ethanol (10 ml) for 4 h to desilylate starting material. The solvent was removed by evaporation and

Table 3. Reactions of the dimethylallyl sulphone (**9**) in aqueous acetic acid

Entry	Additive[a] (mol equiv.)	Temp. (°C)	Time (h)	Products (%) (**9**)	(**10**)
1	None	95	8	100	
2	None[b]	110	8	85	15
3	BPO (0.1)	110	8		100
4	HQ (0.1)	110	8	100	
5	AcOOH (1.5)	110	8		60[c]
6	$ArSO_2H$ (1.0)	110	0.5		100
7	$ArSO_2H$ (1.0)	70	0.5	10	90
8	$ArSO_2Na$ (0.1)	100	0.5	30	70
9	$ArSO_2Na$ (7)	110	10		100
10	$ArSO_2Na$ (0.1) HQ (0.1)	110	8	85	15

[a] $ArSO_2H$ = toluene-*p*-sulphinic acid; HQ = hydroquinone. [b] A.R. acetic acid used. [c] Epoxide of (**10**) also formed (40%).

the residue was partitioned between dichloromethane (25 ml) and water (15 ml). The aqueous layer was separated, re-extracted with dichloromethane (25 ml) and the combined dichloromethane layers were washed with dilute sodium hydroxide and water, dried ($CaCl_2$), and evaporated. The residual oil was chromatographed on silica [eluant: ether (20%)–light petroleum (80%)], crystallisation from ether–light petroleum afforded (E)-3-*trimethylsilylprop*-2-*enyl* p-*tolyl sulphone* (30%), m.p. 52 °C (Found: C, 58.05; H, 7.55, S, 12.05. $C_{13}H_{20}O_2SSi$ requires C, 58.15; H, 7.5; S, 11.95%); δ_H 0.01 (9 H, s, Me_3Si), 2.43 (3 H, s, ArMe), 3.82 (2 H, dd, *J* 7,1 Hz, CH_2SO_2), 5.71 (1 H, dt, *J* 18.5, 1 Hz, =CH), 5.92 (1 H, dt, *J* 18.5, 7 Hz, =CH), 7.33 (2 H, d, ArH), and 7.71 (2 H, d, ArH); δ_C 144.51 (s), 142.73 (d), 135.23 (s), 131.25 (d), 129.37 (d), 128.57 (d), 63.28 (t), 21.49 (q), and −1.84 (q).

(*e*) *Rearrangement of* p-*tolyl* 2-*trimethylsilylbut*-3-*en*-2-*yl sulphone*). The sulphone was subjected to the standard conditions to give a mixture of starting material and product in the ratio 1:9. The latter sulphone was separated by chromatography on silica [eluant: ether (20%)–light petroleum (80%)] and crystallised to give p-*tolyl* 3-*trimethylsilylbut*-2-*enyl sulphone* (from ether–light petroleum), m.p. 64 °C (Found: C, 59.8; H, 7.7; S, 11.15. $C_{14}H_{22}O_2SSi$ requires C, 59.55; H, 7.85; S, 11.35%); δ_H 0.02 (9 H, s, Me_3Si), 1.33 (3 H, d, *J* 2 Hz, =CMe), 2.45 (3 H, s, ArMe), 3.89 (2 H, d, *J* 7.5 Hz, CH_2SO_2), 5.69 (1 H, tq, *J* 7.5, 2 Hz, =CH), 7.31 (2 H, d, ArH), and 7.72 (2 H, d, ArH); δ_C 148.02 (s), 144.40 (s), 135.50 (s), 129.36 (d), 128.49 (d), 123.25 (d), 55.52 (t), 21.47 (q), 14.37 (q), and −2.59 (q).

(*f*) *Rearrangement of* p-*tolyl* 1-*trimethylsilylcyclohex*-2-*enyl sulphone*. The silyl sulphone was treated with three batches of dibenzoyl peroxide (5 mol %) at *t* = 0, 18, and 32 h and worked up after 50 h as described in the general procedure to give a mixture of starting material and product in the ratio 40:60 by n.m.r. spectroscopy. The latter sulphone was purified by the aqueous ethanol treatment described in (*d*) to give p-*tolyl* 3-*trimethylsilylcyclohex*-2-*enyl sulphone* (32%), m.p. 74 °C (from light petroleum) (Found: C, 62.45; H, 7.75; S, 10.55. $C_{16}H_{24}O_2SSi$ requires C, 62.4; H, 7.6; S, 10.4%); δ_H 0.03 (9 H, s, Me_3Si), 1.3—2.1 (6 H, m, ring CH_2), 2.43 (3 H, s, ArMe), 3.74 (1 H, br, $CHSO_2$), 6.04 (1 H, br s, =CH), 7.32 (2 H, d, ArH), and 7.70 (2 H, d, ArH); δ_C 148.46 (s), 144.49 (s), 134.29 (s), 129.34 (d), 129.24 (d), 125.43 (d), 62.73 (d), 26.02 (t), 22.75 (t), 21.55 (q), 20.00 (t), and −2.55 (q).

Reactions of Allylic Sulphones in Aqueous Acetic Acid.—A solution of the allylic sulphone (0.15—0.6 mmol, *ca.* 0.05M) in acetic acid–water (3:2 v/v) under nitrogen was treated as specified in Tables 3 to 5. Aqueous NaOH was added to neutralise the reaction mixture and the product was isolated with ether. Analysis was by n.m.r. spectroscopic comparison with authentic samples of starting materials[24] or products characterised elsewhere in this experimental section.

Table 4. Rearrangements of cyclohex-2-enyl sulphones[a]

Entry	Substrate	Temp. (°C)	Time (h)	Re-covery (%)	Products (%)
1	(**21**; R = Me)	100	8	90	(**22**; R = Me) 100
2	(**21**; R = Me)	100	2	91	(**21**; R = Me) 75, (**22**; R = Me) 25[b]
3	(**21**; R = Me)[c]	100	8	90	(**22**; R = Me, Ar = Ph) 65 (**22**; R = Me, Ar = *p*-Tol) 35
4	(**21**; R = Me)[d]	100	8	50	(**21**; R = Me) 40, (**22**; R = Me) 60
5	(**21**; R = Me)[e]	100	8	58	(**21**; R = Me) 5, (**22**; R = Me) 95
6	(**21**; R = Et)	100	8	91	(**22**; R = Et) 100
7	(**21**; R = $PhCH_2$)	100	8	98	(**22**; R = $PhCH_2$) 100
8	(**25**)	20	8	60	(**26**) 70, (**25**) 30

[a] Solvent AcOH–water (3:2) unless otherwise stated. [b] Ratio unaffected in the presence of hydroquinone (0.1 mol equiv.). [c] With sodium benzenesulphinate (7 mol equiv.). [d] Solvent dimethylformamide–water (1:1). [e] Solvent formamide–water (1:1).

Table 5. Reactions of [1-^{2}H]cyclohex-2-enyl *p*-tolyl sulphone in AcOH–water

Entry	Additive (mol equiv.)	Temp. (°C)	Time (h)	Products (%) [1-^{2}H]-Sulphone (**17**)	[3-^{2}H]-Sulphone (**18**)
1	None	100	8	100	
2	BPO (0.1)	100	8	50	50
3	$ArSO_2Na$ (0.1)	100	8	70	30
4	$ArSO_2Na$ (0.1) HQ (0.1)	100	8	100	
5	$ArSO_2Na$ (1.0)	110	26	50	50

Rearrangement of Allylic Sulphones in the Presence of Sodium Arenesulphinate: Preparative Procedure.—The sulphone (0.02 mol) in AcOH–water (3:2; 150 ml) containing the appropriate sodium arenesulphinate (0.02 mol) was stirred under nitrogen and heated to 100 °C for 8 h. The cooled solution was added to ice-cold aqueous NaOH and extracted with ether. The ethereal solution was washed successively with aqueous NaOH, aqueous HCl, water, and brine. Evaporation of the ether and chromatography of the residue on silica gel [eluant; ether–light petroleum (3:2)] followed by crystallisation gave the sulphone (**22**) indicated. Although the presence of sodium arenesulphinate in these cases is not strictly necessary, its inclusion led to more consistent yields of crystalline product.

(*a*) 3-*Methylcyclohex*-2-*enyl phenyl sulphone* (70%), had m.p. 65 °C (from ether–light petroleum) (Found: C, 66.2; H, 6.85; S, 13.7. $C_{13}H_{16}O_2S$ requires C, 66.05; H, 6.8; S, 13.55%); δ_H 1.35—2.0 (6 H, m, ring CH_2), 1.73 (3 H, br s, =CMe), 3.74 (1 H, br s, 1-H), 5.52 (1 H, br s, 2-H), 7.5—7.93 (5 H, m, Ph).

(*b*) 3-*Methylcyclohex*-2-*enyl* p-*tolyl sulphone* (66%) had m.p. 52 °C (from ether–light petroleum) (Found: C, 67.0; H, 7.35; S,

Table 6. Reactions of 5-t-butylcyclohex-2-enyl *p*-tolyl sulphone in AcOH–water

Entry	$ArSO_2Na$ (mol equiv.)	Temp. (°C)	Time (h)	Products (%) *cis*-Sulphone (**19**)	Products (%) *trans*-Sulphone (**20**)
1	0	110	30	80	20
2	0[a]	110	14	80	20
3	1	110	23	70	30
4	10	110	11.5	60	40[b]
5[c]	1	Reflux	27	60	40[b]
6[d]	1	Reflux	24	60	40[b]

[a] Contained NaBr (10 mol equiv.). [b] Equilibrium mixture.[24] [c] *trans*-Sulphone (**20**) was used. [d] *cis*-Sulphone (**19**) was used.

12.65. $C_{14}H_{18}O_2S$ requires C, 67.15; H, 7.25; S, 12.8%); δ_H 1.35—1.95 (6 H, m, ring CH_2), 1.70 (3 H, s, =CMe), 2.42 (3 H, s, MeAr), 3.70 (1 H, br, 1-H), 5.49 (1 H, brs, 2-H), 7.31 (2 H, d, ArH), and 7.72 (2 H, d, ArH).

(*c*) 3-*Benzylcyclohex*-2-*enyl* p-*tolyl sulphone* (80%), had m.p. 75 °C (from ether–light petroleum) (Found: C, 73.3; H, 6.7; S, 9.45. $C_{20}H_{22}O_2S$ requires: C, 73.6; H, 6.8; S, 9.8%); δ_H 1.35—2.05 (6 H, m, ring CH_2), 2.45 (3 H, s, MeAr), 3.3 (2 H, br s, PhCH_2), 3.77 (1 H, br, 1-H), 5.57 (1 H, br s, 2-H), and 7.0—7.45 and 7.6—7.75 (9 H, m, ArH).

(*d*) 3-*Ethylcyclohex*-2-*enyl* p-*tolyl sulphone* (66%), had m.p. 57 °C (from ethanol–water) (Found: C, 68.35; H, 7.55; S, 12.25. $C_{15}H_{20}O_2S$ requires C, 68.4; H, 7.6; S, 12.2%); δ_H 0.97 (3 H, t, *J* 7.5 Hz, Me), 1.3—2.1 (8 H, m, CH_2), 2.44 (3 H, s, MeAr), 3.72 (1 H, br, 1-H), 5.51 (1 H, br s, 2-H), 7.33 (2 H, d, ArH), and 7.74 (2 H, d, ArH).

Rearrangement of [1-^{2}H]*Cyclohex*-2-*enyl* p-*Tolyl Sulphone*.—The sulphone[24] (0.5 g) was treated with sodium toluene-*p*-sulphinate (250 mg) in AcOH–water at 110 °C according to the above preparative procedure. The product (85%) had m.p. 55—58 °C (from benzene), δ_H 1.4—2.05 (6 H, m, ring CH_2), 2.45 (3 H, s, MeAr), 3.73 ($\frac{1}{2}$ H, br, 1-H), 5.76 (1 H, m, 2-H), 6.09 ($\frac{1}{2}$ H, dt, *J* 10.5, 4.5 Hz, 3-H), 7.35 (2 H, d, ArH), 7.76 (2 H, d, ArH); δ_C 134.67 (t, C-3) and 61.34 (t, C-1); δ_D 3.73 ($\frac{1}{2}$ D, br, 1-D) and 6.11 (12 D, br 3-D).

Similar results were obtained on rearrangement of the sulphone (87 mg) using BPO (5 mg) in CCl_4 (5 ml) under reflux (18 h, argon atmosphere).

The sulphone was recovered unchanged after being heated in AcOH–water (3:2) at 110 °C for 8 h.

Rearrangement of 1-*Methylcyclohex*-2-*enyl t-Butyl Sulphone*.—The sulphone (120 mg) in water–THF (1:1, 2.5 ml) containing lithium iodide (160 mg) was heated under reflux for 8 h. Evaporation, addition of water, and isolation with ether followed by preparative t.l.c. on silica gel [eluant ether–light petroleum (1:1)] gave the product (45 mg) as an oil. Crystallisation of the product from light petroleum afforded 3-*methylcyclohex*-2-*enyl t-butyl sulphone*, m.p. 46 °C (Found: C, 61.0; H, 9.15; S, 14.7. $C_{11}H_{20}O_2S$ requires C, 61.1; H, 9.3; S, 14.8%); δ_H 1.3—2.2 (6 H, m, ring CH_2), 1.46 (9 H, s, Bu^t), 1.78 (3 H, br s, Me), 3.91 (1 H, br, 1-H), and 5.54 (1 H, br s, 2-H).

Under similar conditions 1-methylcyclohex-2-enyl *p*-tolyl sulphone and dimethylallyl *p*-tolyl sulphone were recovered unchanged.

Reaction of 5-*t-Butylcyclohex*-2-*enyl* p-*Tolyl Sulphone with Sodium Toluene*-p-*sulphinate in Aqueous Acetic Acid*.—The sulphone,[24] usually as the *cis–trans* mixture (4:1) but on two occasions as the pure diastereoisomer, was heated in AcOH–water (3:2) under the conditions specified in Table 6. The neutralised product was isolated by extraction with ether and analysed by 300 MHz n.m.r. spectroscopy. Results are given in Table 6.

Similar experiments were carried out using [1-^{2}H]-labelled sulphone as the *cis-trans* (3:2) mixture.[24] Results are listed in Table 7.

Table 7. Reactions of [1-^{2}H]-5-t-butylcyclohex-2-enyl *p*-tolyl sulphone in AcOH–water

Entry	$ArSO_2Na$ (mol equiv.)	Temp. (°C)	Time (h)	Products (%) [1-^{2}H]-Sulphone	Products (%) [3-^{2}H]-Sulphone
1	0	110	44	100	
2	1.3	110	8	*ca.* 95	*ca.* 5
3	1.1	110	23	65	35
4	10	110	11.5	50	50

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