Radical Induced 1,3-Rearrangement–Cyclisations of Some Unsaturated Allylic Sulphones

Thomas A. K. Smith and Gordon H. Whitham *
Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

1,3-Rearrangement–cyclisation of unsaturated allylic sulphones, typified by the conversion of the pentenyl substituted allyl sulphone (**6**) into the cyclic sulphone (**8**), is described. Reaction is considered to occur by a radical chain mechanism involving addition–elimination of $ArSO_2^{\bullet}$. The scope of the reaction has been explored, using various methyl substituted substrates of type (**13**) and other structural variants, and found to be quite general.

The previous paper[1] demonstrated the feasibility of a radical induced addition–cyclisation process of the type (**1**)→(**2**) for the conversion of the allylic ether (**3**) into the hydrobenzofuran (**4**) and related cyclisations. In order to explore further the scope of these reactions, we wanted to prepare substrates (**1**) such that simple carbocyclic products (**2**) would result. It occurred to us that a possible route to such substrates would be the 1,3-rearrangement of the isomeric allylic sulphone (**5**), the latter being, in principle, readily available *via* α-alkylation[2,3] of allyl *p*-tolyl sulphone with an appropriate alkenyl halide. Because the radical induced 1,3-rearrangement of allylic sulphones[3] can take place under similar conditions to the cyclisation (**3**)→(**4**), it was hoped that two stages (**5**)→(**1**)→(**2**) could be telescoped into a 'one-pot' reaction.

Our first attempts centred on 3-*p*-tolylsulphonylocta-1,7-diene (**6**) which should be a favourable case since the ring closure step would correspond to the formation of a 5-membered ring from a hex-5-enyl radical.[4]

After a certain amount of experimentation, the allylic sulphone (**6**) was prepared in 77% yield by alkylation of metallated allyl *p*-tolyl sulphone with 5-bromopent-1-ene (at −50 °C). The sulphone (**6**) was heated in CCl_4 (77 °C) in the presence of dibenzoyl peroxide (BPO) and the progress of the reaction was monitored by ^1H n.m.r. After 1 h the multiplet at δ 3.47 attributable to 3-H in (**6**) had diminished significantly and a new doublet at δ 3.7 assigned to 8-H in 8-*p*-tolylsulphonylocta-1,6-diene (**7**) had appeared. After 3 h this doublet had virtually disappeared and was replaced by a multiplet in the region of δ 3.0 ascribed to CH_2 α to sulphone in the substituted cyclopentane (**8**). Work-up of the product at this stage gave an oil in 93% yield after chromatography. The same material (95%) was obtained after treatment of (**6**) with $ArSO_2Na$–aq. AcOH at 100 °C for 16 h.

The 300 MHz ^1H n.m.r. spectrum of the cyclised product (**8**) showed signals characteristic for the vinyl group, a single allylic proton, and $CHCH_2SO_2Ar$, and indicated that two diastereoisomers were present in the ratio of 3:1.† Confirmation of some of these structural features was provided by the ^1H n.m.r. spectrum of (**8**) after deuterium exchange (NaOD–D_2O, reflux) which showed absence of peaks attributable to CH_2SO_2Ar, *i.e.* indicative of the formation of (**9**). Furthermore deuterium exchange in starting material (**6**) (BuLi, then D_2O) to give (**10**), followed by cyclisation gave product (**11**) which showed no absorption in the allylic proton region of the ^1H n.m.r. spectrum.

On prolonged treatment (24 h) with BPO in CCl_4 under reflux, the well known radical chain addition of CCl_4[6] to the double bond of sulphone (**8**) occurred giving the adduct (**12**). This addition can of course be obviated by using the $ArSO_2Na$–aq. AcOH conditions already mentioned, or by BPO catalysis in alternative solvents (see Experimental section).

For an examination of the scope of the sequential rearrangement–cyclisation of unsaturated allylic sulphones, we prepared a range of methyl substituted compounds of type (**13**), either by alkylation of the appropriate allyl sulphone with the relevant unsaturated alkyl halide or by further methylation of 3-*p*-tolylsulphonylocta-1,7-diene. The behaviour of the products towards radical initiators was then investigated.

The 3-methyl sulphone (**14**) underwent rearrangement–cyclisation to give sulphone (**15**) in reasonable yield as a 5:2 mixture of diastereoisomers using either BPO–CCl_4 or $ArSO_2Na$–aq. AcOH. Thus the 5-ring cyclisation occurs despite the presence of a methyl group at the site of carbon–carbon bond formation.

Sulphone (**16**), derived from methylallyl *p*-tolyl sulphone, underwent efficient conversion into the isomer (**17**), as a 3:1 mixture of diastereoisomers, under either set of reaction conditions.‡ The overall transformation (**16**)→(**17**) was qualitatively faster than (**6**)→(**8**). Apparently the 2-methyl has a favourable influence on the radical addition steps. There is kinetic evidence in the literature for small but significant acceleration of the rate of radical additions to a double bond by a β-methyl.[7] The 3-methyl homologue of (**16**), *i.e.* sulphone (**18**) was also cyclised efficiently to give (**19**).

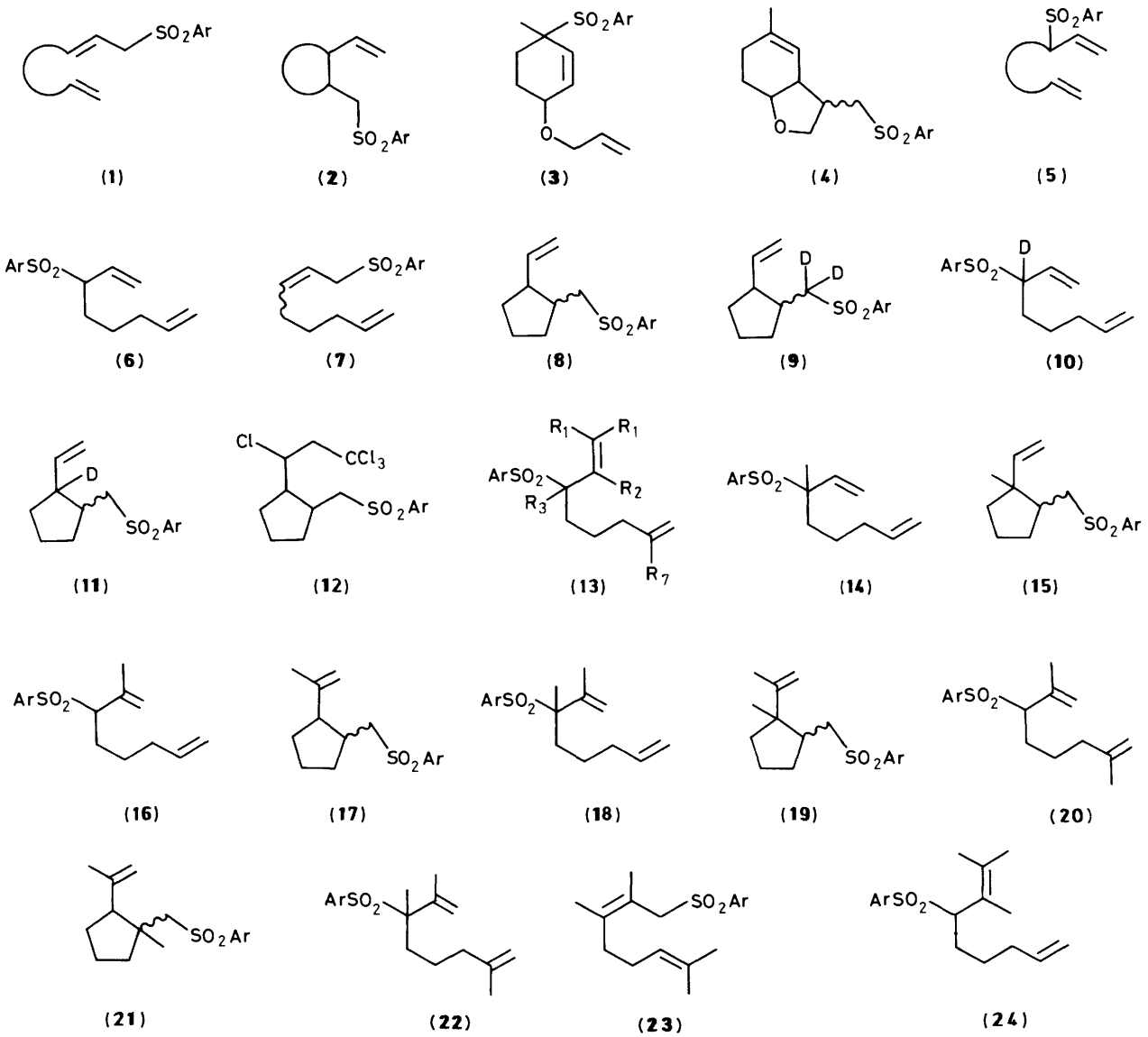
So far, all our successful examples have involved cyclisation *via* addition to a terminal monosubstituted double bond so that the proposed attacking radical in the intramolecular S_H2' reaction was always secondary. We therefore included the 2,7-dimethyl homologue (**20**) in our studies. Cyclisation of the latter to the isomeric sulphone (**21**) showed the feasibility of the intramolecular addition of a tertiary radical centre to the allylic sulphone.

Given the success in formation of a carbon–carbon bond between a quaternary and a tertiary centre for sulphones (**15**), (**19**), and (**21**), we also tried bond formation between two quaternary centres using the sulphone (**22**) as substrate. However, this attempt was unsuccessful and even under the more forcing conditions no cyclised product was isolated. The major material produced was tentatively assigned structure (**23**), the product of 1,3-rearrangement of the allylic sulphone and prototropic isomerisation of the isolated double bond.

The trimethyl substituted sulphone (**24**) was of interest since it was considered that in the 1,3-rearrangement to (**25**), prior to cyclisation, an equilibrium would be set up which favoured (**24**),

† On the basis of Beckwith's findings[5] concerning the preferred mode of cyclisation of 1-substituted hex-5-enyl radicals, the major diastereoisomer is tentatively assigned the *cis*-stereochemistry.

‡ As a prototype substrate, the behaviour of sulphone (**16**) under a range of reaction conditions was also explored (see Experimental section).



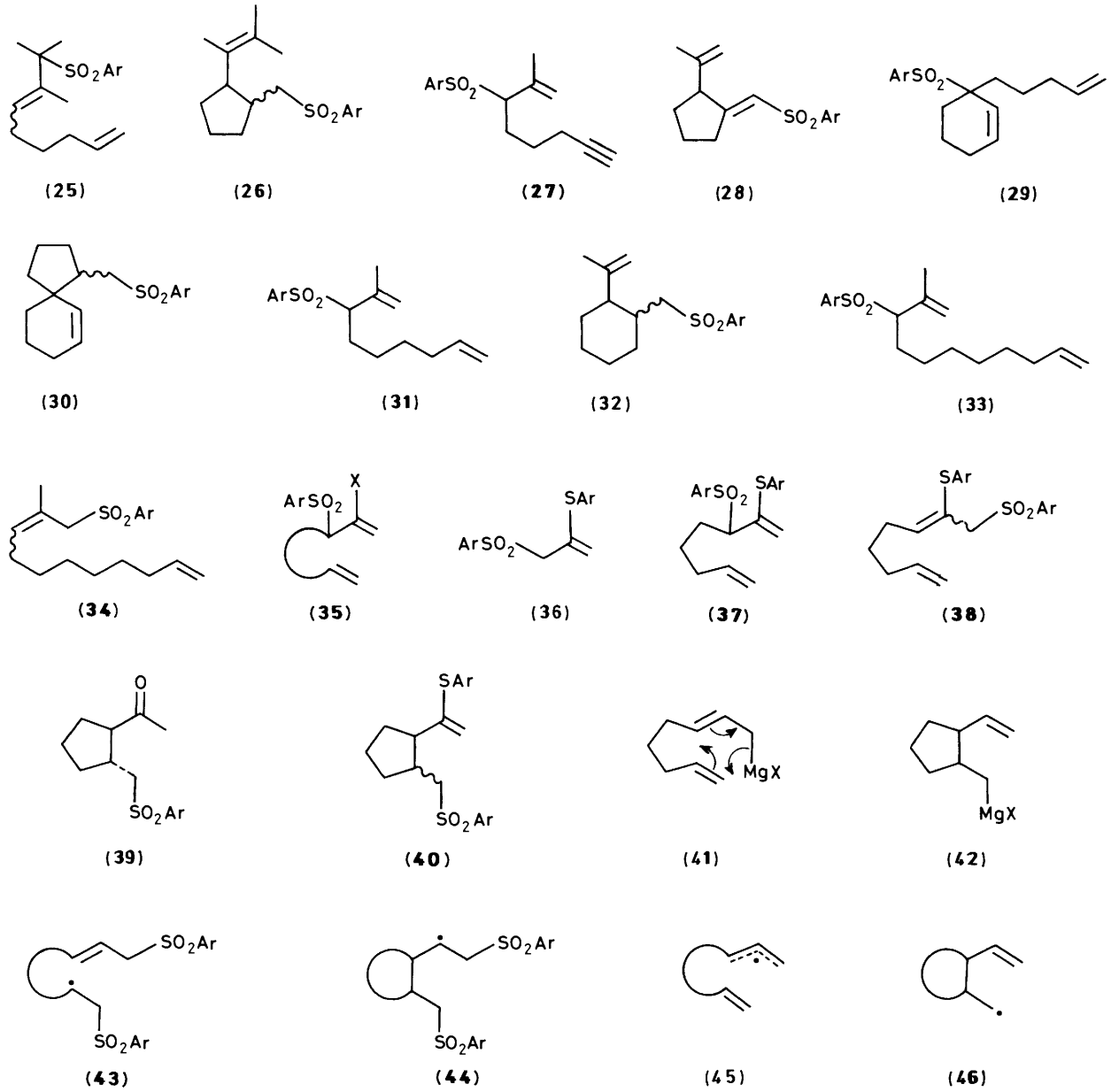
with the more heavily substituted double bond. Nevertheless the cyclopentane (**26**) was obtained in 90% yield using the $ArSO_2Na$–aq. AcOH conditions. Thus the preference for the 5-*exo* mode of cyclisation has favoured reaction *via* sulphone (**25**) rather than the isomer (**24**) for which only the 7-*endo* mode would be available.

Having examined the influence of methyl substitution, we looked at two other structural variants which might lead to 5-membered rings. The acetylenic allylic sulphone (**27**) under the standard BPO-CCl_4 conditions gave a single cyclised vinyl sulphone (80%) considered to be the *E*-isomer (**28**) on the basis of preferred *anti* addition to the acetylene.[8] The pentenyl substituted cyclohexenyl sulphone (**29**) was tried as a possible substrate for spirocyclisation. Treatment with $ArSO_2Na$–aq. AcOH, conditions which lead to 1,3-rearrangement of 1-alkylcyclohex-2-enyl *p*-tolyl sulphones,[9] gave, albeit in only moderate yield (26%), a compound with spectroscopic data consistent with the spiro[5.4]dec-2-ene structure (**30**) (8:1 mixture of the two diastereoisomers).

To show that other ring sizes could be formed, the hex-5-enyl substituted allylic sulphone (**31**) was tested. After treatment with $ArSO_2Na$–aq. AcOH the cyclohexane derivative (**32**), obtained as a 1:1 mixture of diastereoisomers, was isolated in 60% yield. Not surprisingly, the homologous sulphone (**33**) failed to undergo ring closure to an 8-membered ring and only the 1,3-rearranged mixture of allylic sulphones (**34**) was formed.

We next attempted to extend the rearrangement–cyclisation approach to include heteroatom substituted allylic sulphones of type (**35**; X = OR or SR). The alkoxy substituted system turned out to be too acid labile to use,[10] but alkylation * of the thioenol ether (**36**) with 5-bromopent-1-ene gave a mixture of allylic sulphones (**37**) and (**38**) in the ratio 2:1. Apparently some 1,3-rearrangement had occurred subsequent to alkylation. Treatment of this mixture with $ArSO_2Na$–aq. AcOH gave the *trans*-methyl ketone (**39**), identified by comparison with material prepared *via* ozonolysis of sulphone (**17**). We believe that ketone (**39**) is formed *via* the cyclised intermediate (**40**) which is hydrolysed *in situ*; enolisation ensures that the more stable *trans*-isomer (**39**) is produced. In a control experiment it was shown by 4-t-butyl-1-*p*-tolylthiocyclohexene underwent hydrolysis to 4-t-butylcyclohexanone in hot 60% aq. AcOH. Although hydrolysis of thioenol ethers is often found to be

* After completion of our work, alkylations of β-thio substituted allylic sulphones were reported.[11]



difficult, there are precedents for their conversion into ketones in the absence of thiophiles or Lewis acids.[12] Apparently, however, the nearby electron-withdrawing sulphonyl group in the precursors (**37**) and (**38**) reduces their basicity sufficiently to disfavour protonation–hydrolysis prior to cyclisation.

The rearrangement–cyclisation of unsaturated allylic sulphones described in this paper thus appears to have some potential as a synthetic method, given the readily availability of starting materials. A major drawback is that the cyclisation is not stereoselective and a mixture of diastereoisomeric products is generally obtained, but one possible way of circumventing this problem is illustrated by the above preparation of ketone (**39**). The overall transformation (**1**)→(**2**) has close affinity, from a synthetic point of view, with the 'magnesium ene reaction' (**41**)→(**42**) described by Felkin *et al.*[13] and skilfully exploited by Oppolzer.[14]

Although we have not carried out any definitive mechanistic studies on the cyclisation, we favour the radical chain stepwise addition–elimination of $ArSO_2^{\cdot}$ involving (**43**) and (**44**) as intermediates in the generalised conversion (**1**)→(**2**), by analogy with the proposed mechanism for radical induced 1,3-rearrangement of allylic sulphones.[9] Conceivable alternative mechanisms comprising dissociation–recombination of arenesulphonyl radicals with (**45**) and (**46**) as intermediates are not so readily compatible with the radical initiation–inhibition evidence.

Experimental

^1H 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. ^{13}C N.m.r. spectra were obtained on a Bruker AM250 instrument (62.86 MHz) using $CDCl_3$ as solvent. Mass spectra were recorded on a VG Analytical 30F, 16F, or ZAB 1F instrument operating at 70 eV. High resolution spectra (h.r.m.s.) were recorded on the ZAB 1F instrument.

General Procedure for the Monoalkylation of Acyclic Allylic Sulphones.—A solution of the allylic sulphone in 1:1 THF–ether (*ca.* 10 ml per mmol of sulphone) was cooled to −22 °C (CCl_4, CO_2 bath). Butyl-lithium (1.1 equiv.) was added

dropwise *via* syringe, and the colourless solution became yellow–orange. Dry HMPA (2.0 equiv.) was added to this solution and the colour darkened considerably. The mixture was maintained at −22 °C for 20 min, cooled to −50 °C (2:1 CCl_4–isopropyl alcohol, CO_2 bath), and stirred for a further 20 min at this temperature. The alkyl bromide (1.1 equiv.) was added dropwise *via* syringe and the resulting mixture stirred at −50 °C for a further 2 h. Glacial acetic acid (0.5 ml per mmol sulphone) was then added *via* syringe and the deep orange colour of the solution was immediately discharged. The mixture was allowed to warm to room temperature and diluted two-fold with ether. After dilution with water, the organic layers were separated and washed successively with dilute aqueous sodium hydroxide, dilute aqueous sodium hydrogen sulphite, dilute hydrochloric acid, water, and brine. The organic extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give, in most cases, the crude alkylated sulphone as a pale yellow solid after trituration of the crude reaction mixture with light petroleum. The following sulphones were prepared by this method.

3-p-*Tolylsulphonylocta*-1,7-*diene* (**6**). Prepared using 3-*p*-tolylsulphonylpropene (1.0 g, 5.1 mmol) and 5-bromopentene (0.65 ml). Recrystallisation gave the *sulphone* (**6**) (0.95 g, 71%) as needles, m.p. 59—60 °C (from pentane) (Found: C, 68.15; H, 7.75. $C_{15}H_{20}O_2S$ requires C, 68.15; H, 7.65%); $\delta_H(CDCl_3)$ 1.23—2.25 (6 H, complex CH_2), 2.47 (3 H, s, MeAr), 3.47 (1 H, br dt, *J* 8 and 4 Hz, 3-H), 4.88—5.83 (6 H, complex, 2 × HC=CH_2), 7.32 (2 H, d, ArH), and 7.73 (2 H, d, ArH); *m*/*z* (NH_3 d.c.i.) 282 (100%, $M^+ + 18$), 265 (40, $M^+ + 1$), and 139 (18, $ArSO^+$).

2-*Methyl*-3-p-*tolylsulphonylocta*-1,7-*diene* (**16**). Prepared using 2-methyl-3-*p*-tolylsulphonylpropene (3.0 g, 0.14 mmol) and 5-bromopentene (1.84 ml). Recrystallisation gave the *sulphone* (**16**) (3.65 g, 93%) as needles, m.p. 47—48 °C (from pentane) (Found: C, 69.4; H, 8.3. $C_{16}H_{22}O_2S$ requires C, 69.05; H, 8.00%); $\delta_H(CDCl_3)$ 1.26—1.45 (4 H, complex, CH_2), 1.77 (3 H, s, 2-Me), 1.80—2.14 (2 H, complex, 6-H_2), 2.44 (3 H, s, MeAr), 3.52 (1 H, dd, *J* 12 and 3.5 Hz, 3-H), 4.72 (1 H, s, 1-H), 4.92—5.02 (3 H, complex, 8-H_2, 1-H), 5.73 (1 H, m, 7-H), 7.31 (2 H, d, ArH), and 7.70 (2 H, d, ArH); *m*/*z* (NH_3 c.i.) 296 (100%, $M^+ + 18$) and 123 (29, ArS^+).

2,7-*Dimethyl*-3-p-*tolylsulphonylocta*-1,7-*diene* (**20**). Prepared using 2-methyl-3-*p*-tolylsulphonylpropene (0.50 g, 2.35 mmol) and 5-bromo-2-methylpentene (0.25 ml) to give the crude sulphone (0.79 g) as a pale oil containing some (< 10%) starting material. Purification on silica gel using 4:1 light petroleum–ether as eluant gave the sulphone (**20**) (0.53 g, 71%) as a colourless oil; $\delta_H(CDCl_3)$ 1.25—2.12 (6 H, complex, CH_2), 1.68 (3 H, s, 7-Me), 1.78 (3 H, s, 2-Me), 2.45 (3 H, s, MeAr), 3.53 (1 H, dd, *J* 13 and 3 Hz, 3-H), 4.63 (1 H, s, C=CH), 4.69 (1 H, s, C=CH), 4.73 (1 H, s, C=CH), 5.03 (1 H s, C=CH), 7.31 (2 H, d, ArH), and 7.71 (2 H, d, ArH); *m*/*z* (NH_3 c.i.) 310 (100%, $M^+ + 18$) and 293 (20, $M^+ + 1$).

2,3-*Dimethyl*-4-p-*tolylsulphonylnona*-2,8-*diene* (**24**). Prepared using 2,3-dimethyl-4-*p*-tolylsulphonylbut-2-ene[10] (0.20 g, 0.84 mmol) and 5-bromopentene (0.2 ml) to give the crude sulphone (**24**) (0.26 g) as a pale oil which was used without purification for subsequent reactions; $\delta_H(CDCl_3)$ 1.16 (3 H, s, 1-Me), 1.16—1.39 (2 H, complex, CH_2), 1.56 (3 H, s, 1-Me), 1.69 (3 H, s, 2-Me), 1.89—2.14 (4 H, complex CH_2), 2.40 (3 H, s, MeAr), 4.03 (1 H, dd, *J* 13 and 4 Hz, 4-H), 4.94 (2 H, complex, 9-H_2), 5.70 (1 H, m, 8-H), 7.25 (2 H, d, ArH), and 7.63 (2 H, d, ArH); *m*/*z* (NH_3 d.c.i.) 324 (60%, $M^+ + 18$), 307 (7, $M^+ + 1$), and 151 (100).

2-*Methyl*-3-p-*tolylsulphonyloct*-1-*en*-7-*yne* (**27**). Prepared using 2-methyl-3-*p*-tolylsulphonylpropene (1.43 g, 6.8 mmol) and 5-bromopentyne (1.48 ml). Recrystallisation gave the *sulphone* (**27**) (1.80 g, 96%) as needles, m.p. 76—77 °C (from pentane) (Found: C, 69.4; H, 7.5. $C_{16}H_{20}O_2S$ requires C, 69.55; H, 7.30%); $\delta_H(CDCl_3)$ 1.35—2.27 (6 H, complex, CH_2), 1.78 (3 H, s, 2-Me), 1.92 (1 H, t, *J* 3 Hz, 8-H), 2.43 (3 H, s, MeAr), 3.53 (1 H, dd, *J* 12 and 4 Hz, 3-H), 4.73 (1 H, s, 1-H), 5.03 (1 H, s, 1-H), 7.30 (2 H, d, ArH), and 7.71 (2 H, d, ArH); *m*/*z* (NH_3 c.i.) 294 (100%, $M^+ + 18$) and 139 (40, $ArSO^+$).

2-*Methyl*-3-p-*tolylsulphonylnona*-1,8-*diene* (**31**). Prepared using 2-methyl-3-*p*-tolylsulphonylpropene (1.0 g, 4.7 mmol) and 6-bromohexene (0.71 ml). Purification on silica gel using 4:1 light petroleum–ether as eluant gave the sulphone (**31**) (1.20 g, 86%) as a colourless oil; $\delta_H(CDCl_3)$ 1.16—2.12 (8 H, complex, CH_2), 1.78 (3 H, s, 2-Me), 2.45 (3 H, s, MeAr), 3.51 (1 H, dd, *J* 12 and 4 Hz, 3-H), 4.72 (1 H, s, 1-H), 4.95 (3 H, complex, 9-H_2, 1-H), 5.75 (1 H, m, 8-H), 7.30 (3 H, d, ArH), and 7.71 (2 H, d, ArH); *m*/*z* (NH_3 d.c.i.) 310 (100%, $M^+ + 18$) and 283 (20, $M^+ + 1$).

2-*Methyl*-3-p-*tolylsulphonylundeca*-1,10-*diene* (**33**). Prepared using 2-methyl-3-*p*-tolylsulphonylpropene (0.5 g, 2.35 mmol) and 8-bromo-octene (0.21 ml). Filtration of an ethereal solution of the crude sulphone through a small plug of silica gel followed by evaporation gave the sulphone (**33**) (0.76 g, 93%) as a colourless oil which was used without further purification; $\delta_H(CDCl_3)$ 1.20—2.15 (12 H, complex, CH_2), 1.78 (3 H, s, 2-Me), 2.45 (3 H, s, MeAr), 3.50 (1 H, dd, *J* 13 and 4 Hz, 3-H), 4.70(1 H, s, 1-H), 4.95 (3 H, complex, 11-H_2, 1-H), 5.78 (1 H, complex, 10-H), 7.30 (2 H, d, ArH), and 7.70 (2 H, d, ArH); *m*/*z* (NH_3 d.c.i.) 338 (95%, $M^+ + 18$), 321 (30, $M^+ + 1$), and 165 (100).

3-*Deuterio*-3-p-*tolylsulphonylocta*-1,7-*diene* (**10**). Butyl-lithium (0.3 ml of a 1.54M solution in hexane, 1.1 equiv.) was added to a solution of the sulphone (**6**) (117 mg, 0.44 mmol) in 1:1 THF–ether (8 ml) and cooled to −78 °C. The resulting yellow-orange solution was stirred at −78 °C for 2 h and then deuterium oxide (1 ml) was added slowly *via* syringe. The mixture was allowed to warm to room temperature, diluted with ether (15 ml), and the ethereal solution washed successively with dilute aqueous hydroxide, dilute hydrochloric acid, water, and brine. The dried ($MgSO_4$) solution gave the crude sulphone (**10**) (107 mg, 91%) as a pale solid, m.p. 45—47 °C, which was used without further purification. The 300 MHz n.m.r. spectrum was very similar to that for the sulphone (**6**), but without the resonance at δ 3.47.

Methylation of Acyclic Allylic Sulphones.—Methylation of acyclic allylic sulphones was carried out by dropwise addition of a solution of butyl-lithium (2.0 equiv.) in hexane to a solution of the allylic sulphone and methyl iodide (3.0 equiv.) in THF–ether at −78 °C. After 1 h at −78 °C and warming to 20 °C, aqueous ammonium chloride (1 ml, saturated solution) was added and the product isolated with ether. The following sulphones were prepared in this way.

3-*Methyl*-3-p-*tolylsulphonylocta*-1,7-*diene* (**14**). A pale solid was obtained from the crude reaction mixture after trituration with light petroleum. Recrystallisation gave the *sulphone* (**14**) as needles (82%), m.p. 63.5—64.5 °C (from pentane) (Found: C, 69.25; H, 8.2. $C_{16}H_{22}O_2S$ requires C, 69.05; H, 8.00%); $\delta_H(CDCl_3)$ 1.27—2.13 (6 H, complex, CH_2), 1.35 (3 H, s, 3-Me), 2.46 (3 H, s, MeAr), 5.00 (3 H, complex, 1-H, 8-H_2), 5.35 (1 H, d, *J* 11 Hz, 1-H), 5.76 (1 H, m, 7-H), 5.90 (1 H, dd, *J* 15 and 11 Hz, 2-H), 7.30 (2 H, d, ArH), and 7.66 (2 H, d, ArH); *m*/*z* (NH_3 d.c.i.) 296 (100%, $M^+ + 18$).

2,3-*Dimethyl*-3-p-*tolylsulphonylocta*-1,7-*diene* (**18**). The sulphone was obtained as a pale oil (97%) and was used without purification for subsequent reactions; $\delta_H(CDCl_3)$ 1.17—2.25 (6 H, complex, CH_2), 1.42 (3 H, s, 3-Me), 1.90 (3 H, s, 2-Me), 2.45 (3 H, s, MeAr), 4.76 (1 H, s, 1-H), 5.00 (2 H, m, 8-H_2), 5.12 (1 H, s, 1-H), 5.78 (1 H, m, 7-H), 7.28 (2 H, d, ArH), and 7.68 (2 H, d, ArH); *m*/*z* (NH_3 d.c.i.) 310 (100%, $M^+ + 18$).

2,3,7-*Trimethyl*-3-p-*tolylsulphonylocta*-1,7-*diene* (**22**). The sulphone was isolated as a pale yellow oil (88%) after an ethereal solution of the crude reaction mixture was filtered through silica

Table 1. Cyclisation of unsaturated allylic sulphones using BPO–CCl_4 (Method A)

Entry	Substrate	Time (h)	Product	Yield (%)
1	(**6**)	3	(**8**)	93[a]
2	(**6**)	24	(**12**)	95[b]
3	(**10**)	3	(**11**)	95[b]
4	(**14**)	16	(**15**)	80[b]
5	(**16**)	3	(**17**)	90[b]
6	(**18**)	16	(**19**)	50[b]
7	(**24**)	16	(**26**)	60[b]
8	(**27**)	21	(**28**)	80[b]

[a] Isolated. [b] Estimated by n.m.r.

Table 2. Cyclisation of unsaturated allylic sulphones using NaTs-aq. AcOH (Method B)

Entry	Substrate	Time (h)	Product	Yield (%)
1	(**6**)	16	(**8**)	95[a]
2	(**14**)	40	(**15**)	53[b]
3	(**16**)	16	(**17**)	95[a]
4	(**18**)	40	(**19**)	60[b]
5	(**24**)	22	(**26**)	90[b]
6	(**27**)	70	(**28**)	80[a]
7	(**31**)	16	(**32**)	60[b]
8	(**29**)	92	(**30**)	26[a]
9	(**20**)	16	(**21**)	73[a]

[a] Isolated. [b] Estimated by n.m.r.

Table 3. Cyclisation of unsaturated allylic sulphones using BPO in various solvents (Method C)

Entry	Substrate	Solvent	Time (h)	Product	Yield (%)
1	(**6**)	C_6D_6	18	(**8**)	80[a]
2	(**27**)	Bu^{t}OH	16	(**28**)	80[b]
3	(**27**)	C_6H_{12}	16	(**28**)	80[a]
4	(**16**)	Bu^{t}OH	16	(**17**)	91[b,c]
5	(**16**)	C_6H_{12}	16	(**17**)	93[b,d]
6	(**16**)	C_6D_6	5	(**17**)	95[a,c]

[a] Estimated by n.m.r. [b] Isolated. [c] 3:1 Mixture of diastereoisomers. [d] 3:2 Mixture of diastereoisomers.

gel, and used without purification for subsequent reactions. $\delta_H(CDCl_3)$ 1.43 (3 H, s, 3-Me), 1.70 (3 H, s, 7-Me), 1.80—2.25 (6 H, complex, CH_2), 1.93 (3 H, s, 2-Me), 2.45 (3 H, s, MeAr), 4.65 (1 H, s, 8-H), 4.72 (1 H, s, 8-H/1-H), 4.74 (1 H, s, 1-H/8-H), 5.15 (1 H, s, 1-H), 7.27 (2 H, d, ArH), and 7.67 (2 H, d, ArH); *m/z* (NH_3 d.c.i.) 324 (40%, $M^+ + 18$), 307 (14, $M^+ + 1$), and 151 (100).

3-(*Pent-4′-enyl*)-3-p-*tolylsulphonylcyclohexene* (**29**). Prepared using essentially the same procedure using 5-brompentene as the alkylating agent. The sulphone was obtained as a pale oil and, after filtration in ether solution through a plug of silica gel, was used without further purification for subsequent reactions; $\delta_H(CDCl_3)$ 1.40—2.15 (12 H, complex, CH_2), 2.46 (3 H, s, MeAr), 4.90 (2 H, complex, 5′-H_2), 5.72 (2 H, complex, 1- and 2-H), 6.12 (1 H, complex, 4′-H), 7.33 (2 H, d, ArH), and 7.76 (2 H, d, ArH); *m/z* (NH_3 d.c.i.) 322 (38%, $M^+ + 18$), 305 (12, $M^+ + 1$), and 148 (100).

Rearrangement and Cyclisation of Allylic Sulphones.—One-pot rearrangement and cyclisation of certain allylic sulphones was carried out using essentially the procedure described in the previous paper[1] (Methods A and B) or by Method C, described below. The results are presented in Tables 1, 2, and 3. Spectroscopic and other data for the products are given below.

General Procedure for Radical Cyclisation Using Dibenzoyl Peroxide in Deuteriobenzene, Cyclohexane, or t-Butyl Alcohol. [Method C).—Dibenzoyl peroxide (*ca.* 2 mg) was added to a solution of the substrate (10—100 mg) in a suitable solvent (*i.e.* deuteriobenzene, cyclohexane, or t-butyl alcohol). The resulting mixture was transferred to a 5 mm n.m.r. tube and heated to 85 °C (oil bath temperature). In favourable cases the reaction could be monitored by 60 MHz n.m.r. ignoring solvent resonances. When judged to be complete the excess of solvent was removed under reduced pressure and the residues were taken up in ether. The ether solution was washed with dilute aqueous sodium hydroxide, water, and brine. After drying ($MgSO_4$) the solvent was removed under reduced pressure to give products, usually as pale oils. Alternatively the solvent could be removed from the crude reaction mixture under reduced pressure and the residues taken up in deuteriochloroform. Examination of the 60 MHz n.m.r. spectrum in this solvent allowed the extent of the reaction to be determined. If the reaction was not complete, it could be restarted according to the procedure described above.

1-*Vinyl*-2-p-*tolylsulphonylmethylcyclopentane** (**8**). The *sulphone* was isolated as a colourless oil after chromatography on silica gel using 5:1 light petroleum–ether as eluant (Found: C, 68.4; H, 7.7. $C_{15}H_{20}O_2S$ requires C, 68.15; H, 7.60%); $\delta_H(CDCl_3)$ 1.25—2.13 (6 H, complex, CH_2), 2.41 (1 H, br m, 2-H), 2.46 (3 H, s, MeAr), 2.65 (1 H, br m, 1-H), 2.83—3.33 (2 H, complex, CH_2SO_2Ar), 4.97 (2 H, m, CH=CH_2), 5.56 (1 H, m, C*H*=CH_2), 7.35 (2 H, d, ArH), and 7.80 (2 H, d, ArH); *m/z* (NH_3 c.i.) 282 (55%, $M^+ + 18$), 265 (83, $M^+ + 1$), and 109 (100, $M^+ - ArSO_2$).

A sample of sulphone (**8**) was deuteriated by heating under reflux (16 h) with sodium deuteroxide in deuterium oxide (0.01M). Isolation with ether gave a colourless oil, the ^1H n.m.r. spectrum of which was very similar to that above but without the multiplet at δ 2.83—3.33.

1-(1,3,3,3-*Tetrachloropropyl*)-2-p-*tolylsulphonylmethylcyclopentane* (**12**). Prolonged treatment of the allylic sulphone (**6**) with BPO–CCl_4 (Method A) (24 h), followed by standard work-up gave the chlorinated product (**12**); $\delta_H(CDCl_3)$ 1.50—2.05 (6 H, complex, CH_2), 2.48 (3 H, s, MeAr), 2.50—2.75 (2 H, complex, 1- and 2-H), 3.05—3.52 (4 H, complex, CH_2SO_2Ar, CH_2CCl_3), 4.58 (1 H, m, CHCl), 7.38 (2 H, d, ArH), and 7.83 (2 H, d, ArH); $\delta_C(CDCl_3)$ 21.65 (q), 23.98 (t), 26.25 (t), 32.66 (t), 37.04 (d), 46.74 (d), 56.53 (t), 59.40 (d), 61.32 (t), 96.67 (s), 127.87 (d), 130.02 (d), 136.93 (s), and 114.74 (s); *m/z* (NH_3 c.i.) 436 (100%, $M^+ + 18$).

1-*Deuterio*-1-*vinyl*-2-p-*tolylsulphonylmethylcyclopentane* (**11**). The sulphone was obtained from the rearrangement–cyclisation of the deuteriated allylic sulphone (**10**) as a colourless oil. The 300 MHz ^1H n.m.r. spectrum was very similar to that for 1-vinyl-2-*p*-tolylsulphonylmethylcyclopentane (**8**), but without a resonance at δ 2.65.

1-*Methyl*-1-*vinyl*-2-p-*tolylsulphonylcyclopentane* (**15**). The sulphone was obtained as a 5:2 mixture of diastereoisomers as a pale oil after chromatography on silica gel using 5:1 light petroleum–ether as eluant; $\delta_H(CDCl_3)$ 1.05 (3 H, s, 1-Me), 1.38—2.15 (6 H, complex, CH_2), 2.33 (1 H, m, 2-H), 2.46 (3 H, s, MeAr), 2.85 (1 H, m, CH_2SO_2Ar, minor isomer), 3.08 (1 H, m, CH_2SO_2Ar, major isomer), 4.95 (2 H, complex, CH=CH_2), 5.62

* The standard IUPAC nomenclature used for this compound should be 1-*p*-tolylsulphonylmethyl-2-vinylcyclopentane. However, throughout the Experimental section, the non-standard name has been retained due to the numbering used in the n.m.r. data.

(1 H, dd, *J* 17 and 11 Hz, C*H*=CH_2, minor isomer), 5.68 (1 H, dd, *J* 17 and 11 Hz, C*H*=CH_2, major isomer), 7.35 (2 H, complex, ArH), and 7.81 (2 H, complex, ArH); *m/z* (NH_3 d.c.i.) 296 (90%, M^+ + 18), 139 (23, $ArSO^+$), and 123 (100, ArS^+).

1-*Propen-2-yl*-2-*tolylsulphonylmethylcyclopentane* (**17**). The *sulphone* was obtained as a pale oil after chromatography on silica gel using 4:1 light petroleum–ether as eluant. A 3:1 ratio of diastereoisomers was formed by methods A and B, and a 3:2 ratio of diastereoisomers was formed by method C (Found: C, 68.8; H, 8.2. $C_{16}H_{22}O_2S$ requires C, 69.00; H, 7.95%); $\delta_H(CDCl_3)$ 1.55 (3 H, s, MeC=C), 1.60—2.25 (7 H, complex, CH_2, 2-H), 2.46 (3 H, s, MeAr), 2.55 (1 H, m, 1-H), 2.66—3.00 (2 H, complex, CH_2SO_2Ar), 4.61 (1 H, br s, C=CH, minor isomer), 4.63 (1 H, br s, C=CH, major isomer), 4.71 (1 H, br s, C=CH, minor isomer), 4.82 (1 H, br s, C=CH, major isomer), 7.35 (2 H, d, ArH), and 7.78 (2 H, d, ArH); *m/z* (NH_3 d.c.i.) 296 (100%, M^+ + 18), 279 (27, M^+ + 1), and 123 (95, ArS^+).

1-*Methyl*-1-*propen*-2-*yl*-2-p-*tolylsulphonylmethylcyclopentane* (**19**). The *sulphone* was isolated as a pale oil after chromatography on silica gel using 4:1 light petroleum–ether as eluant (Found: C, 70.15; H, 8.45. $C_{17}H_{24}O_2S$ requires C, 69.85; H, 8.30%); $\delta_H(CDCl_3)$ 1.03 (3 H, s, 1-Me), 1.26—2.25 (7 H, complex, CH_2, 2-H), 1.61 (3 H, s, MeC=C), 2.46 (3 H, s, MeAr), 2.68 (1 H, dd, *J* 15 and 12 Hz, $CHSO_2Ar$), 2.93 (1 H, d, *J* 15 Hz, $CHSO_2Ar$), 4.65 (1 H, s, C=CH), 4.77 (1 H, br s, C=CH), 7.35 (2 H, d, ArH), and 7.69 (2 H, d, ArH); *m/z* (NH_3 c.i.) 310 (100%, M^+ + 18) and 293 (14, M^+ + 1).

2-*Methyl*-1-*propen*-2-*yl*-2-p-*tolylsulphonylmethylcyclopentane* (**21**). The *sulphone* was isolated as a colourless oil after chromatography on silica gel using 4:1 light petroleum–ether as eluant (as a 3:2 mixture of diastereoisomers) (Found: C, 69.7; H, 8.3. $C_{17}H_{24}O_2S$ requires C, 69.80; H, 8.30%); $\delta_H(CDCl_3)$ 1.08 (3 H, s, 2-Me, minor isomer), 1.41 (3 H, s, 2-Me, major isomer), 1.58—1.92 (6 H, complex, CH_2), 2.23 (1 H, complex, 1-H), 2.45 (3 H, s, MeAr), 3.00 (2 H, s, CH_2SO_2Ar, major isomer), 3.0, 3.35 (2 H, AB system, 2 × 'd,' *J* 15 Hz, CH_2SO_2Ar, minor isomer), 4.67 (1 H, br s, C=CH, both isomers), 4.84 (1 H, br s, C=CH, major isomer), 4.87 (1 H, br s, C=CH, minor isomer), 7.32 (2 H, d, ArH), and 7.78 (2 H, d, ArH); *m/z* (e.i. probe) 292 (1%, M^+) (Found: M^+, 292.1496. $C_{17}H_{24}O_2S$ requires *M*, 292.1497).

1-(2′-*Methylbut*-2′-*en*-3′-*yl*)-2-p-*tolylsulphonylmethylcyclopentane* (**26**). The sulphone was obtained as a pale oil after chromatography on silica gel using 4:1 light petroleum–ether as eluant; $\delta_H(CDCl_3)$ 1.37—2.05 (6 H, complex, CH_2), 1.50 (6 H, s, 2 × 2′-Me), 1.64 (3 H, s, 3′-Me), 2.38 (2 H, complex, 1- and 2-H), 2.45 (3 H, s, MeAr), 2.85 (1 H, dd, *J* 15 and 12 Hz, $CHSO_2Ar$), 3.07 (1 H, dd, *J* 15 and 3 Hz, $CHSO_2Ar$), 7.33 (2 H, d, ArH), and 7.78 (2 H, d, ArH); *m/z* (NH_3 c.i.) 340 (100%, M^+ + 18) and 323 (30, M^+ + 1).

1-*Propen*-2-*yl*-2-p-*tolylsulphonylmethylenecyclopentane* (**28**). The sulphone was obtained as a pale oil after chromatography on silica gel using 4:1 light petroleum–ether as eluant: $\delta_H(CDCl_3)$ 1.56 (3 H, s, MeC=C), 1.60—1.90 (4 H, complex, CH_2), 2.45 (3 H, s, MeAr), 2.50—3.25 (3 H, complex, 1-H, 3-H_2), 4.75 (1 H, br s, C=CH_2), 4.88 (1 H, br s, C=CH_2), 6.12 (1 H, m, C=C*H*SO_2Ar), 7.33 (2 H, d, ArH), and 7.76 (2 H, d, ArH); *m/z* (NH_3 d.c.i.) 294 (75%, M^+ + 18), 277 (100, M^+ + 1), and 139 (18, $ArSO^+$).

1-*Propen*-2-*yl*-2-p-*tolylsulphonylmethylcyctohexane* (**32**). The sulphone was obtained as a pale oil (*ca.* 1:1 mixture of diastereoisomers) after chromatography on silica gel using 4:1 light petroleum–ether as eluant; $\delta_H(CDCl_3)$ 1.16—2.10 (8 H, complex, CH_2), 2.32 (3 H, s, MeC=C), 2.40 (2 H, complex, 1- and 2-H), 2.46 (3 H, s, MeAr), 2.73 (1 H, dd, *J* 14 and 10 Hz, $CHSO_2Ar$, isomer A), 2.93 (1 H, br d, *J* 14 Hz, $CHSO_2Ar$, isomer B), 3.08 (1 H, dd, *J* 14 and 10 Hz, $CHSO_2Ar$, isomer B), 3.24 (1 H, dd, *J* 14 and 1.5 Hz, $CHSO_2Ar$, isomer A), 4.54 (1 H, s, C=CH, isomer B), 4.62 (1 H, s, C=CH, isomer A), 4.72 (1 H, br s, C=CH, isomer A), 4.82 (1 H, s, C=CH, isomer B), 7.35 (2 H, d, ArH), and 7.77 (2 H, d, ArH); *m/z* (NH_3 d.c.i.) 310 (38%, M^+ + 18) and 293 (100, M^+ + 1).

7-p-*Tolylsulphonylmethylspiro*[5.4]*dec*-1-*ene* (**30**). The sulphone was isolated as a colourless oil (26%), an 8:1 mixture of diastereoisomers, after chromatography on silica gel using 4:1 light petroleum–ether as eluant (Found: C, 71.0; H, 8.15. $C_{18}H_{24}O_2S$ requires C, 71.0; H, 7.95%); $\delta_H(CDCl_3)$ 1.36—2.12 (12 H, complex, CH_2), 2.46 (3 H, s, MeAr), 2.90 (1 H, dd, *J* 14.5 and 11 Hz, $CHSO_2Ar$), 3.12 (1 H, dd, *J* 14.5 and 2.5 Hz, $CHSO_2Ar$), 5.10 (1 H, br d, *J* 10 Hz, 2-H, minor isomer), 5.35 (1 H, br d, *J* 10 Hz, 2-H, major isomer), 5.64 (1 H, m, 3-H, major isomer), 5.73 (1 H, m, 3-H, minor isomer), 7.37 (2 H, d, ArH), and 7.78 (2 H, d, ArH); $\delta_C(CDCl_3)$ 19.45 (t, minor isomer), 20.51 (t, major isomer), 21.19 (t, minor isomer), 21.54 (t, major isomer), 22.41 (q), 25.18 (t, major isomer), 26.57 (t, minor isomer), 29.13 (t, minor isomer), 30.83 (t, major isomer), 35.00 (t, major isomer), 37.55 (t, minor isomer), 40.33 (t, major isomer), 43.46 (d, major isomer), 44.31 (d, minor isomer), 46.62 (s, major isomer), 46.80 (s, minor isomer), 58.06 (t, minor isomer), 59.13 (t, major isomer), 127.75 (d), 129.73 (d), 130.70 (d), 134.22 (d), 137.17 (s), and 144.28 (s) (Found: M^+, 304.1498. $C_{18}H_{24}O_2S$ requires *M*, 304.1497); *m/z* (e.i.) 304 (4%, M^+); *m/z* (NH_3 d.c.i.) 322 (60%, M^+ + 18) and 149 (100).

Reaction of 2,3,7-*Trimethyl*-3-p-*tolylsulphonylocta*-1,7-*diene* (**22**) *with Sodium* p-*Tolylsulphinate* (*Method B*).—The sulphone (**23**) was obtained as the major product, apparently as a single diastereoisomer, after chromatography on silica gel using 4:1 light petroleum–ether as eluant; $\delta_H(CDCl_3)$ 1.18 (3 H, s, Me), 1.53 (3 H, s, Me), 1.63 (3 H, s, Me), 1.69 (3 H, s, Me), 1.89 (4 H, m, CH_2CH_2), 2.38 (3 H, s, MeAr), 3.78 (2 H, s, CH_2SO_2Ar), 5.00 (1 H, br t, *J* 6 Hz, C=CH), 7.23 (2 H, d, ArH), and 7.66 (2 H, d, ArH).

A minor product (<5%) was assigned the structure 2,3,7-trimethyl-1-p-tolylsulphonylocta-2,6-diene (**23**); $\delta_H(CDCl_3)$ 1.28 (3 H, s, Me), 1.38 (2 H, m, CH_2), 1.70 (3 H, s, Me), 1.78 (3 H, s, Me), 1.98 (4 H, m, CH_2C=C, CH_2C=C), 2.43 (3 H, s, MeAr), 3.86 (2 H, s, CH_2SO_2Ar), 4.65 (1 H, s, C=CH), 4.73 (1 H, s, C=CH), 7.30 (2 H, d, ArH), and 7.72 (2 H, d, ArH). Reduced reaction times gave a greater proportion of this material.

3-p-*Tolylsulphonyl*-2-p-*tolylthiopropene* (**36**).—A solution of *p*-thiocresol (3.19 g, 0.025 mol), 3-*p*-tolylsulphonylpropyne (5.0 g, 0.025 mol), and triethylamime (0.25 ml) in benzene (100 ml) was stirred at room temperature. After 2 h the benzene solution was washed successively with dilute aqueous sodium hydroxide (50 ml), dilute hydrochloric acid (50 ml), water (50 ml), and brine (50 ml). The benzene solution was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a pale yellow solid (8.61 g). Recrystallisation from dichloromethane–light petroleum gave the *sulphone* as needles (5.3 g, 65%), m.p. 64—65 °C (Found: C, 64.1; H, 5.75. $C_{17}H_{18}O_2S$ requires C, 64.10; H, 5.70%); $\delta_H(CDCl_3)$ 2.30 (3 H, s, *Me*C_6H_4S), 2.45 (3 H, s, *Me*$C_6H_4SO_2$), 3.85 (2 H, s, CH_2SO_2Ar), 5.03 (1 H, s, C=CH), 5.27 (1 H, s, C=CH), 7.20 [6 H, complex, Ar(S), Ar(SO_2)], and 7.70 [2 H, d, Ar(SO_2)]; *m/z* (NH_3 d.c.i.) 336 (10%, M^+ + 18), 319 (100, M^+ + 1), and 318 (50, M^+).

Alkylation of 3-p-*Tolylsulphonyl*-2-p-*tolylthiopropene* (**36**).—A sample of the thioenol ether (**36**) was treated with 5-bromopentene according to the general alkylation procedure already described. The pale oil obtained in 95% yield after standard work-up was shown by 300 MHz ^1H n.m.r. to contain the desired sulphone (**37**) and its [1,3]allylic sulphone rearranged isomer (**38**) (*ca.* 2:1); the two isomers could not be separated by chromatography, and were used without further purification for subsequent reactions; $\delta_H(CDCl_3)$ 2.06—2.41 (6 H, complex, CH_2), 2.45 (3 H, s, MeC_6H_4S, minor isomer), 2.48 (3 H, s, MeC_6H_4S, major isomer), 2.62 (3 H, s, $MeC_6H_4SO_2$),

3.75 (1 H, dd, *J* 12 and 5 Hz, $CHSO_2Ar$, major isomer), 4.05 (2 H, s, CH_2SO_2Ar, minor isomer), 4.90 (1 H, s, 1-H, major isomer), 5.1—5.25 (2 H, m, 8-H, both isomers), 5.45 (1 H, s, 1-H, both isomers), 5.89 (1 H, m, 7-H, both isomers), 6.21 (1 H, t, *J* 8 Hz, 3-H, minor isomer), and 7.12—7.90 (8 H, complex Ar); *m/z* (NH_3 d.c.i.) 404 (25%, $M^+ + 18$), 387 (40, $M^+ + 1$), and 231 (100).

2-p-*Tolylsulphonylmethylcyclopentyl Methyl Ketone* (**39**).—A solution of the thioenol ethers (**37**) and (**38**) (95.3 mg, 0.25 mmol), and sodium *p*-tolylsulphinate (0.5 g, 7 equiv.) in 60% aqueous acetic acid (10 ml) was heated to 95 °C for 16 h. The mixture was cooled, diluted with water (10 ml), and extracted with ether (2 × 10 ml). The ether extracts were washed with dilute aqueous sodium hydroxide until neutral, water (10 ml), and brine (10 ml). The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a pale oil. The crude product was treated with sodium *p*-tolylthiolate in ethanol to convert the reaction by-product, toluene-*p*-thiolsulphonate into di-*p*-tolyldisulphide. Chromatography on silica gel using 3:2 ether–light petroleum as eluant gave the *ketone* (**39**) as a colourless oil (30 mg) (Found: C, 64.3; H, 7.4. $C_{15}H_{20}O_3S$ requires C, 64.25; H, 7.20%); $\nu_{max.}(CHCl_3)$ 1 705 cm^{-1} (CO); $\delta_H(CDCl_3)$ 1.50—2.08 (6 H, complex, CH_2), 2.22 (3 H, s, MeCO), 2.47 (3 H, s, MeAr), 2.63 (1 H, m, 1- or 2-H), 2.85 (1 H, m, 1- or 2-H), 3.13 (2 H, AB quartet split by 2-H, CH_2SO_2Ar), 7.36 (2 H, d, ArH), and 7.59 (2 H, d, ArH); *m/z* (NH_3 d.c.i.) 298 (100%, $M^+ + 18$) and 281 (20, $M^+ + 1$).

Ozonolysis of 1-*Propen*-2-*yl*-2-p-*tolylsulphonylmethylcyclopentane* (**17**).—A solution of the sulphone (**17**) (100 mg) in dry methanol (10 ml) was ozonolysed at −78 °C for 30 min until the solution was pale blue. Dimethyl sulphide (1 ml) was then added and the solution left stirring at −78 °C for a further 1 h. The solvent and excess of dimethyl sulphide were removed under reduced pressure and the residues taken up in ether (20 ml). The ether solution was washed with dilute aqueous hydroxide (10 ml), dilute hydrochloric acid (10 ml), water (10 ml), and brine (10 ml). After drying ($MgSO_4$), the solvent was removed under reduced pressure to give a pale oil (80 mg). This material was not identified, but had the following ^1H n.m.r. data; $\delta_H(CDCl_3)$ 1.20 (s), 1.30 (s), 1.40—2.20 (complex), 2.45 (s, MeC_6H_4), 3.15—3.90 (complex), 7.35 (d, *J* 8 Hz, Ar), and 7.75 (d, *J* 8 Hz, Ar).

The oil was unstable and, with time, underwent partial conversion into the keto sulphone (**39**).

Alternatively, the oil obtained above was dissolved in dilute aqueous sodium hydroxide (10 ml) and the mixture heated to 100 °C for 2 h. After cooling the mixture was extracted with ether (2 × 10 ml), and the ether extracts were washed with dilute hydrochloric acid (10 ml), water (10 ml), and brine (10 ml). The ether extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a pale oil (50 mg). The 300 MHz ^1H n.m.r. spectrum of this material was identical with that of the keto sulphone (**39**) obtained *via* the thioneol ethers (**37**) and (**38**).

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