Further Radical Induced Cyclisations of Unsaturated Sulfones

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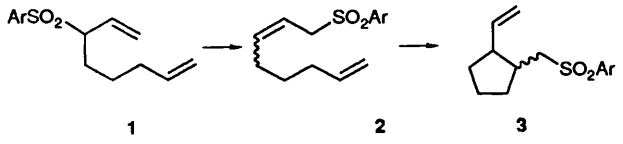
Radical induced cyclisations of unsaturated sulfones by the *endo*-5-*exo*- and the *exo*-5-*exo*-*ipso*-modes are described. Thus the unsaturated allylic sulfones **4**, **6** and **8** underwent cyclisation to the cyclopentyl sulfones **5**, **7**, and **9** and **10** respectively, while the unsaturated vinylic sulfones **14** and **15** were isomerised to the cyclopentylmethyl sulfones **17** and **18** respectively.

In our previous papers on this topic[1] and in related studies by other workers[2] examples have all been of the type illustrated by the case shown in Scheme 1. Here 1-*p*-tolylsulfonylocta-2,7-



1 2 3

Scheme 1

diene **2**, itself produced *in situ* by radical induced 1,3-rearrangement[3] of 3-*p*-tolylsulfonylocta-1,7-diene **1**, underwent cyclisation to the vinylcyclopentane **3** in greater than 90% yield on treatment either with benzoyl peroxide (BPO) in CCl_4 under reflux, or with sodium *p*-toluenesulfinate in aqueous acetic acid at 100 °C. Thus, with respect to the ring being formed, both exocyclic addition to the isolated double bond and exocyclic addition to the double bond of the allylic sulfone has occurred. The cyclisation shown can therefore be described as an *exo*-5-*exo*-process. We also showed that the homologous process of *exo*-6-*exo*-cyclisation could be achieved.

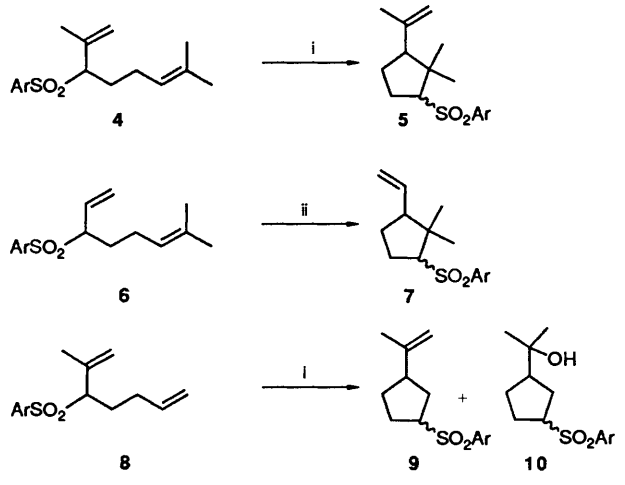
The incentive behind the work described in the present paper was to investigate how far the scope of such reactions could be widened to include endocyclic processes, and whether cyclisation by *ipso*-substitution with unsaturated vinyl sulfones was feasible. As will be seen, the scope for such modifications turns out to be limited, for alkyl substituted systems. The following paper is concerned with activated systems, where an electron withdrawing substituent is present on the 2-position of the allylic sulfone grouping, and a wider variety of possible cyclisation types can be achieved.

Scheme 2 summarises successful examples found for the *endo*-5-*exo*-process. The substrates **4**, **6** and **8** were all prepared from the appropriate allylic sulfone by mono-alkylation using standard chemistry as described in the Experimental section.

Sulfone **4** was designed so that addition of $ArSO_2$ radicals should occur at the less substituted end of the isolated double bond giving a tertiary radical which could then cyclise by a 5-*exo*-process onto the double bond of the 1,3-rearranged allylic sulfone giving the cyclised product **5**. Sulfone **5** was in fact obtained, as a mixture of diastereoisomers, in 68% yield on treatment of **4** with sodium toluene-*p*-sulfinate in aqueous acetic acid at 100 °C. We have argued previously[1] that these conditions are a way of generating *p*-tolylsulfonyl radicals and hence of initiating the chain addition elimination sequence.

In a similar manner, but less efficiently, the analogous sulfone **6**, without the methyl group at the 2-position, underwent rearrangement–cyclisation to give the cyclic sulfones **7**, in 51% yield, on treatment with BPO–CCl_4 under reflux.

Finally, in this series, the possible cyclisation of the unsaturated sulfone **8** was explored. In this case, unlike sulfones **4** and **6**, where the presence of the trisubstituted double bond was expected to favour the 5-*endo*-process, addition of $ArSO_2$ radical to the unsubstituted end of the isolated double bond might be expected to be preferred. However the secondary radical thereby formed could only cyclise either by a 6-*endo*-process onto the allylic sulfone before 1,3-rearrangement, or by a 4-*exo*-process after 1,3-rearrangement. Neither of these modes of cyclisation is particularly favourable and, apparently, reversible addition of *p*-tolylsulfonyl radicals to the isolated double bond of **8** can occur leading, *via* attack at the substituted end, to 5-*endo*-cyclisation. Thus the products obtained from treatment of sulfone **8** with sodium toluene-*p*-sulfinate in aqueous acetic acid at 100 °C, in addition to the 1,3-rearranged isomer of **8**, are assigned structures **9** and **10** obtained in 9 and 25% yields respectively. The tertiary alcohol **10** is considered to have been derived by acid-catalysed hydration of the double bond in **9**.

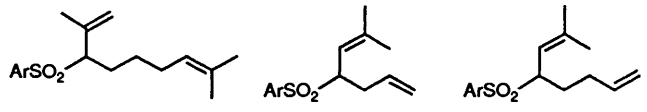


Scheme 2 *Reagents*: i, *p*-TsNa–aq. AcOH, 100 °C; ii, BPO–CCl_4, heat

An attempt was also made to effect an *endo*-6-*exo*-cyclisation using the sulfone **11**, containing one extra methylene group in the side chain than the lower homologue **4**. However treatment of **11** with BPO in either CCl_4 or Bu^{t}OH under reflux gave only the 1,3-rearranged allylic sulfone, while sodium toluene-*p*-sulfinate in aqueous acetic acid gave material considered to have been derived by hydration of the C^7–C^8 double bond. Apparently the known lower rate of cyclisation of hept-6-enyl compared to hex-5-enyl radicals[4] is sufficient to tip the balance against six membered-ring formation.

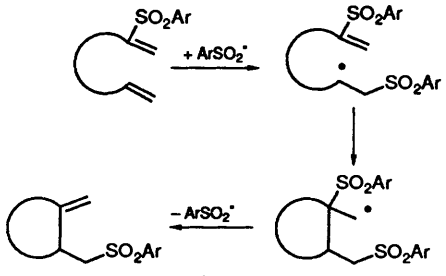
As a further variant, the possibility of cyclisation by the *exo*-5-*endo*- and the *exo*-6-*endo*-modes was explored using the sulfones **12** and **13** as test cases. The substitution pattern shown was chosen because it was known that the presence of the *gem*-dimethyl substituent would disfavour 1,3-shift to the allylic sulfone isomer.[3] It was also considered that the *gem*-dimethyl

grouping would not unduly hinder cyclisation as the analogous formation of a bond between adjacent secondary and tertiary centres had already been achieved in the *exo–exo*-mode.[1] In the event, however, compounds **12** and **13** turned out to be relatively stable under the normal conditions of radical initiation and under more forcing conditions no cyclised products were identified.



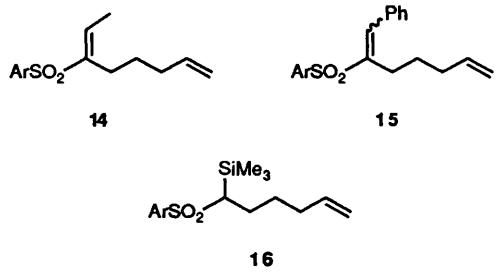
11 **12** **13**

The second possibility that we wished to explore was one in which the cyclisation step involved attack on a vinyl sulfone at the carbon atom bearing the sulfonyl substituent, *i.e.* leading to overall *ipso*-substitution as in Scheme 3. *ipso*-Substitution in both intermolecular[5] and intramolecular[6] reactions of activated vinyl stannanes is well precedented, and *ipso*-substitution involving attack of isopropyl radicals on an activated vinyl sulfone has been reported.[7]



Scheme 3

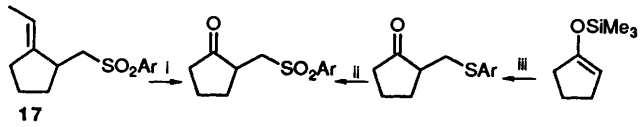
Two possible candidates for an *exo*-5-*exo*-*ipso*-cyclisation, the sulfones **14** and **15**, were prepared. In the first case, **14**, this was achieved by alkylation of allyl-*p*-tolyl sulfone with 1-bromopent-4-ene followed by treatment of the product with triethylamine in CH_2Cl_2 to complete isomerisation to the vinyl sulfone. In the second case, **15** was formed as the product of a Peterson olefination[8] involving treatment of the silyl sulfone **16** successively with butyllithium and then benzaldehyde.



14 **15**

16

The radical cyclisation of sulfone **14** was then attempted under standard BPO–CCl_4 conditions. The major product, obtained in 63% yield, was assigned structure **17**, *i.e.* that expected from *ipso*-cyclisation, on the basis of NMR spectroscopic data, and the structure was confirmed by the transformations summarised in Scheme 4. The cyclic sulfone was

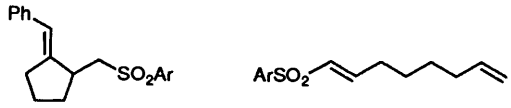


17

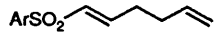
Scheme 4 *Reagents*: i, O_3–MeOH–Me_2S; ii, oxone; iii, $ArSCH_2Cl$–$TiCl_4$

obtained essentially as one isomer (approx. 20:1 ratio), tentatively assigned the configuration shown in **17** since this would minimise steric interactions between adjacent *p*-tolylsulfonylmethyl and ethylidene substituents.

It was hoped that the presence of the phenyl substituent in the unsaturated sulfone **15** would facilitate the *ipso*-cyclisation process compared to the methyl analogue **14** owing to the known favourable effect of a β-phenyl on addition of alkyl radicals to alkenes.[9] In practice disappointing yields were obtained and, for example, treatment of **15** with sodium toluene-*p*-sulfinate in aq. AcOH gave only 39% yield of a compound assigned structure **18** on the basis of comparison of spectroscopic data found with that of the methyl analogue **17**.



18 **19**



20

Attempts were also made to persuade the unsaturated vinyl sulfones **19** and **20** to undergo *ipso*-cyclisation by *exo*-7-*endo*- and *exo*-5-*endo*-processes, respectively. However, treatment of either **19** or **20**, prepared as described in the Experimental section, with sodium toluene-*p*-sulfinate in aq. AcOH gave a complex mixture of products and in neither case were signals typical of alkene protons for 3-*p*-tolylsulfonylmethylcycloheptene, from **19**, or for 3-*p*-tolylsulfonylmethylcyclopentene, from **20**, observed in the respective NMR spectra.

Experimental

^{1}H NMR spectra were recorded on Varian Gemini (200 MHz) or Bruker WH300 (300 MHz) instruments, *J* values are given in Hz. Mass spectra were recorded on VG Analytical 30F, 16F, or ZAB 1F instruments.

General Procedure for the Monoalkylation of Allylic Sulfones.—A solution of the allylic sulfone in 1:1 THF–ether was cooled to −20 °C (CCl_4–CO_2 bath). Butyllithium (1.1 equiv.) was added dropwise *via* syringe followed by dry HMPA (hexamethylphosphoramide) (2.0 equiv.). The resulting mixture was maintained at −20 °C for 30 min then cooled to −70 °C and stirred for a further 30 min at this temperature. The alkyl halide (1:1 equiv.) was added *via* syringe and the resulting mixture was stirred at −70 °C until no starting sulfone was present (by TLC). Glacial acetic acid (0.5 cm^3 per mmol) was then added, the mixture was allowed to warm to room temperature then diluted two-fold with ether. After addition of water, the organic layer was separated and was washed successively with dilute aqueous sodium hydroxide, dilute aqueous sodium bisulfite, dilute hydrochloride acid, water and brine. The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure to give the crude alkylated sulfones as oils.

2,7-*Dimethyl*-3-(p-*tolylsulfonyl*)*octa*-1,6-*diene* **4**. The *sulfone* **4** was prepared from 2-methyl-3(*p*-tolylsulfonyl)prop-1-ene (0.21 g) and 1-iodo-4-methylpent-3-ene[10] (2.1 equiv.) by the general procedure as needles, m.p. 50.5–52 °C (from pentane) (0.202 g, 69%) after chromatography on silica gel using 4:1 light petroleum–ether as eluent. (Found: C, 69.7; H, 8.55. $C_{17}H_{24}O_2S$ requires C, 69.8; H, 8.25%); $\delta_H(CDCl_3)$ 1.54 (3 H, s, C=CMe) 1.67 (3 H, s, C=CMe), 1.79 (3 H, s, C=CMe), 1.86–2.09 (4 H, m, 4-H and 5-H), 2.45 (3 H, s, Me-C_6H_4-) 3.54 (1 H, dd, *J* 3.2, 11.2, 3-H) [absent in the ^{1}H NMR spectrum of 3-deuterio-2,7-di-

methyl-3-(*p*-tolylsulfonyl)octa-1,6-diene, see below], 4.72 (1 H, s, 1-H), 5.04 (1 H, br s, 6-H), 5.06 (1 H, s, 1-H), 7.31 (2 H, d, *J* 8, Ar) and 7.71 (2 H, d, *J* 8, Ar); $\nu_{max}(CCl_4)/cm^{-1}$ 1640 (C=C), 1315, 1145 (SO_2) and 905; *m/z* (NH_2 c.i.) 316 (100%, $M^+ + 18$) and 293 (23%, $M^+ + 1$).

7-*Methyl*-3-(p-*tolylsulfonyl*)*octa*-1,6-*diene* **6**. The sulfone **6** was prepared from 3-(*p*-tolylsulfonyl)prop-1-ene (0.2 g) and 1-iodo-4-methylpent-3-ene (1.2 equiv.) by the general procedure as an oil (0.085 g, 30%) after chromatography on silica gel using 4:1 light petroleum–ether as eluent; $\delta_H(CDCl_3)$ 1.50 (3 H, s, C=Me), 1.60 (3 H, s, C=CMe), 1.70–2.25 (4 H, m, 4-H and 5-H) 2.40 (3 H, s, Me-C_6H_4-), 3.30 (1 H, br t, *J* 9, 3-H), 4.70–5.90 (4 H, m, 1-H, 2-H and 6-H), 7.16 (2 H, d, *J* 8, Ar) and 7.56 (2 H, d, *J* 8, Ar); *m/z* (NH_3 d.c.i.) 296 (64%, $M^+ + 18$), 279 (100%, $M^+ + 1$) and 139 (37%, $ArSO^+$).

The sulfone **6** sometimes contained small amounts of the isomeric vinyl sulfone [identified by a quartet at δ 6.78 (1 H) in the ^1H NMR spectrum] but this impurity did not affect the subsequent reaction.

2-*Methyl*-3-(p-*tolylsulfonyl*)*hepta*-1,6-*diene* **8**. The sulfone **8** was prepared from 2-methyl-3-(*p*-tolylsulfonyl)prop-1-ene (0.21 g) and 4-bromobut-1-ene (0.12 cm^3) by the general procecure as needles, m.p. 36–38 °C (from pentane) (0.17 g, 65%) after chromatography on silica gel using 3:1 light petroleum–ether as eluent; $\delta_H(CDCl_3)$ 1.78 (3 H, s, 2-Me), 1.90–2.20 (4 H, m, 4-H and 5-H), 2.44 (3 H, s, Me-C_6H_4-), 3.55 (1 H dd, *J* 11.7, 2.4, 3-H), 4.72 (1 H, s, 1-H), 4.96–5.06 (2 H, m, 7-H), 5.01 (1 H, s, 1-H), 5.65–5.78 (1 H, m, 6-H), 7.31 (2 H, d, *J* 8, Ar) and 7.71 (2 H, d, *J* 8, Ar); $\nu_{max}(CCl_4)/cm^{-1}$ 1635 (C=C), 1320, 1145 (SO_2) and 910; *m/z* (NH_3 d.c.i.) 282 (100%, $M^+ + 18$), 265 (28%, $M^+ + 1$) and 109 (58%, $M^+ - ArSO_2$).

3-*Deuterio*-2,7-*dimethyl*-3-(-*tolylsulfonyl*)*octa*-1,6-*diene*. Butyllithium (0.07 cm^3 of a 1.7 mol dm^{-3} solution in hexane, 1.2 equiv.) was added to a solution of sulfone **8** (30 mg) in 1:1 THF–ether cooled to −20 °C. The resulting solution was stirred at this temperature for 30 min then cooled to −70 °C and stirred for a further 20 min. Deuterium oxide (0.1 cm^3) was added and the reaction mixture was allowed to warm to room temperature. Ether was added and the organic layer was washed with dilute aqueous sodium hydroxide, dilute hydrochloric acid, water and brine. The organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to give the sulfone as an oil. Filtration of an ethereal solution of the sulfone through a plug of silica gel followed by removal of solvent under reduced pressure gave the product as a clear oil (27 mg, 90%). The 300 MHz spectrum of the deuterated sulfone was very similar to that of the sulfone **4** but without the resonance at δ 3.54.

General Procedure for Radical Cyclisation using Dibenzoyl Peroxide in Carbon Tetrachloride, Cyclohexane, tert-*Butanol or Chlorobenzene* (*Method A*).—Dibenzoyl peroxide (*ca.* 5 mg) was added to a solution of the sulfone (20–70 mg) in a suitable solvent. The resulting mixture was transferred to a 5 mm NMR tube and heated to 80 °C for carbon tetrachloride, *tert*-butanol or cyclohexane or 135 °C for chlorobenzene (oil bath temperatures). The reaction could be monitored by ^1H NMR. If the reaction time exceeded 24 h, fresh dibenzoyl peroxide was added and the reaction restarted. When the reaction was complete the cooled solution was diluted with ether, washed with dilute sodium hydroxide solution, water and brine then dried ($MgSO_4$). Removal of solvent under reduced pressure gave an oil that was usually purified by chromatography.

General Procedure for Radical Cyclisation using Sodium Toluene-p-*sulfinate in Aqueous Acetic Acid* (*Method B*).—To a stirred solution, or suspension of the substrate in 60% aqueous acetic acid (*ca.* 25 cm^3 mol^{-1}) was added sodium toluene-*p*-sulfinate (usually 8 equiv.) and the resulting mixture was heated to *ca.* 100 °C (oil bath temperature) for 20 h. After cooling the mixture was diluted with water and extracted into ether (×2). The combined ether extracts were washed with dilute sodium hydroxide solution, water and brine. Drying ($MgSO_4$) and evaporation of solvent under reduced pressure gave the product as an oil that was usually purified by chromatography.

Details of products and yields of cyclisation reactions of unsaturated allylic sulfones **4** and **6** are given in Table 1.

2,2-*Dimethyl*-1-(*propen*-2′-*yl*)-3-(p-*tolylsulfonyl*)*cyclopentane* **5**. The crude reaction product from experiment 4, Table 1, was shown (by ^1H NMR) to be a mixture of the sulfone **5** and toluene-*p*-thiosulfonate. This mixture was taken up in ethanol and treated with potassium toluene-*p*-thiolate to convert toluene-*p*-thiolsulfonate to di(*p*-tolyl)disulfide. Chromatography on silica gel using 3:1 light petroleum–ether as eluent gave a 3:1 mixture of diastereoisomers of the *sulfone* **5** as needles, m.p. 57–58 °C (from pentane) (Found: C, 69.65; H, 8.45. $C_{17}H_{24}O_2S$ requires C, 69.8; H, 8.25%); $\delta_H(CDCl_3)$ 1.07 (3 H, s, 2-Me, major isomer), 1.16 (3 H, s, 2-Me, minor isomer), 1.32 (3 H, s, 2-Me, minor isomer), 1.50 (3 H, s, 2-Me, major isomer), 1.60–2.28 (4 H, m, 4-H and 5-H), 1.75 (3 H, s, 2′-Me), 2.43 (3 H, s, Me-C_6H_4), 2.49 (1 H, dd, *J* 6, 9, 1-H), 3.15 (1 H, dd, *J* 8, 9, 3-H), 4.66 (1 H, br s, 3′-H, major isomer), 4.72 (1 H, br s, 3′-H, minor isomer), 4.88 (1 H, br s, 3′-H, major isomer), 4.98 (1 H, br s, 3′-H, minor isomer), 7.33 (2 H, d, *J* 8, Ar) and 7.75 (2 H, d, *J* 8, Ar); $\nu_{max}(CCl_4)/cm^{-1}$ 2970, 1690 (C=C), 1598 (Ar), 1305 and 1140 (SO_2); *m/z* (NH_3 d.c.i.) 310 (100%, $M^+ + 18$), 293 (22%, $M^+ + 1$) and 137 (53%, $M^+ - ArSO_2$).

2,2-*Dimethyl*-3-(p-*tolylsulfonyl*)-1-*vinylcyclopentane* **7**. The sulfone **7** was isolated from reaction 7, Table 1, after chromatography on silica gel using 3:1 light petroleum–ether as eluent as a 3:1 mixture of diastereoisomers as an oil; $\delta_H(CDCl_3)$ 1.03 (3 H, s, 2-Me, major isomer), 1.14 (3 H, s, 2-Me minor isomer), 1.23 (3 H, s, 2-Me, minor isomer), 1.45 (3 H, s, 2-Me, major isomer), 1.48–2.18 (4 H, m, 4-H and 5-H), 2.45 (3 H, s, Me-C_6H_4-) 2.45–2.57 (1 H, m, 1-H), 3.17 (1 H, t, *J* 8, 3-H), 4.95–5.15 (2 H, m, C=CH_2), 5.58–5.75 (1 H, m, –CH=C), 7.34 (2 H, d, *J* 8, Ar) and 7.76 (2 H, d, *J* 8, Ar); $\nu_{max}(CCl_4)/cm^{-1}$ 1635 (C=C), 1320, 1145 (SO_2) and 915; *m/z* (NH_3 d.c.i.) 296 (100%, $M^+ + 18$), 279 (24%, $M^+ + 1$) and 123 (42%, $M^+ - ArSO_2$).

1-*Deuterio*-2,2-*dimethyl*-1-(*propen*-2′-*yl*)-3-(p-*tolylsulfonyl*)-*cyclopentane*. The sulfone was isolated from reaction 5, Table 1, as a mixture of diastereoisomers (3:1) after chromatography on silica gel using 3:1 light petroleum–ether as eluent as an oil.

The 300 MHz NMR spectrum of the deuterated sulfone closely resembled that of sulfone **5** but without the resonance at δ 2.49.

3-*Deuterio*-2,2-*dimethyl*-1-(*propen*-2′-*yl*)-3-(p-*tolylsulfonyl*)-*cyclopentene*. The sulfone was prepared from sulfone **5** (15 mg) and deuterium oxide (0.05 cm^3) using essentially the same procedure as described above for 3-deuteriated **4**. PLC using 4:1 light petroleum–ether as eluent gave the deuterated sulfone (10.5 mg, 70%) as an oil. The 300 MHz ^1H NMR spectrum was similar to that of sulfone **5** but the resonance at δ 3.15 was significantly reduced in intensity (corresponding to 50% deuterium incorporation). The ratio of diastereoisomers (as assessed from the resonances between δ 4.65 and 5.00) was 2:1 in favour of what previously had been the minor isomer.

2,8-*Dimethyl*-3-(p-*tolylsulfonyl*)*nona*-1,7-*diene* **11**. The sulfone **11** was prepared from 3-(*p*-tolylsulfonyl)prop-1-ene (0.19 g) and 1-iodo-5-methylhex-4-ene[11] (1.2 equiv.) by the general procedure as an oil (0.15 g, 49%) after chromatography on silica gel using 4:1 light petroleum–ether as eluent; $\delta_H(CDCl_3)$ 1.57 (3 H, s, C=CMe), 1.63 (3 H, s, C=CMe), 1.75 (3 H, s, C=CMe), 1.13–2.15 (6 H, complex, 4-H, 5-H and 6-H), 2.40 (3 H, s, Me-C_6H_4-) 3.38 (1 H, dd, *J* 5, 11, 3-H), 4.60 (1 H, br s, 1-H), 4.90 (1 H, br s, 1-H), 4.96 (1 H, br s, 7-H), 7.17 (2 H, d, *J* 8, Ar) and 7.61 (2 H, d, *J* 8, Ar).

Table 1 Cyclisation of unsaturated allylic sulfones **4** and **6**

Entry	Substrate	Method	Time (h)	Product	Yield[a] (%)
1	**4**	A(CCl_4)	8	**5**	58[b]
2	**4**	A(C_6H_{12})	28	**5**	54[b]
3	**4**	A(Bu^{t}OH)	36	**5**	30[b]
4	**4**	B	16	**5**	68[c]
5	3-deuterio **4**	B	15	1-deuterio **5**	45
6	**6**	A(Bu^{t}OH)	18	**7**	—[d]
7	**6**	A(CCl_4)	18	**7**	51

[a] Yield after chromatography. [b] 1,3-Rearranged sulfone also formed. [c] After KOH/*p*-TolSH treatment. [d] Yield not recorded.

Table 2 Cyclisation of sulfone **14**

Entry	Method	Time (h)	Yield[a] of **17** (%)
1	A(CCl_4)	26	63
2	A(Bu^{t}OH)	75	30
3	B	21	72[b]

[a] Yield after chromatography. [b] After KOH/*p*-TolSH treatment.

Attempted Cyclisation of Sulfone **11**.—Treatment of sulfone **11** with benzoyl peroxide in either carbon tetrachloride or *tert*-butanol (Method A) or with sodium toluene-*p*-sulfinate in 60% aqueous acetic acid (Method B), gave (by NMR) a 2:1 mixture of diastereoisomers of 2,8-dimethyl-1-(*p*-tolylsulfonyl)nona-2,7-diene; $\delta_H(CCl_4)$ 0.90–2.10 (6 H, m, 4-H, 5-H and 6-H), 1.50 (3 H, s, C=CMe), 1.60 (3 H, s, C=CMe), 1.66 (3 H, s, C=CMe), 2.38 (3 H, s, Me-C_6H_4-), 3.50 (2 H, s, 1-H, major isomer), 3.58 (2 H, s, 1-H, minor isomer), 4.75–5.15 (2 H, m, 2-H and 7-H), 7.18 (2 H, d, *J* 8, Ar) and 7.62 (2 H, d, *J* 8, Ar).

Attempted Cyclisation of Sulfone **8**.—A mixture of the sulfone **8** (41.5 mg) and sodium toluene-*p*-sulfinate (220 mg, 6.5 equiv.) was heated in 60% aqueous acetic acid at 95 °C for 36 h (Method B). Chromatography of the crude product on silica gel using 4:1 light petroleum–ether followed by 1:1 light petroleum–ether as eluents gave two sets of products. The faster-running material was shown by ^{1}H NMR spectroscopy to be a mixture of two products: (*a*) 2-methyl-1-(*p*-tolylsulfonyl)hepta-2,6-diene; the sulfone was obtained in 5.3% yield and was identified by the following features in the ^{1}H NMR spectrum: $\delta_H(CDCl_3)$ 1.80 (3 H, s, 2-Me), 2.49 (3 H, s, Me-C_6H_4-), 3.75 (2 H, s, 1-H), 4.90–5.00 (2 H, m, 7-H), 5.12 (1 H, t, *J* 7, 3-H), 5.71 (1 H, m, 6-H), 7.33 (2 H, d, *J* 8, Ar) and 7.75 (2 H, d, *J* 8, Ar); (*b*) 3-(*p*-tolylsulfonyl)-1-(propen-2′-yl)cyclopentane **9**; the cyclopentane **9** was obtained in 9.2% yield as a mixture of diastereoisomers. The structural assignment was based on the following features in the ^{1}H NMR spectrum: $\delta_H(CDCl_3)$ 1.71 (3 H, s, 2′-Me), 2.49 (3 H, s, Me-C_6H_4-), 2.65 (1 H, m, 1-H), 3.58 (1 H, m, 3-H), 4.65–4.80 (2 H, m, C=CH_2) 7.38 (2 H, d, *J* 8, Ar) and 7.79 (2 H, d, *J* 8, Ar). The more polar material (11 mg, 25%) was assigned as a mixture of diastereoisomers of 1-(2′-hydroxyprop-2′-yl)-3-(*p*-tolylsulfonyl)cyclopentane **10**; $\delta_H(CDCl_3)$ 1.25 (6 H, s, 2 × 2′-Me), 1.62–2.25 (7 H, m, 1-H, 2-H, 4-H and 5-H), 2.50 (3 H, s, Me-C_6H_4-), 3.52 (1 H, m, 3-H), 7.35 (2 H, d, *J* 8, Ar) and 7.80 (2 H, d, *J* 8, Ar); $\nu_{max}(CHCl_3)/cm^{-1}$ 3500br (OH), 1598 (Ar), 1300 and 1145 (SO_2), *m*/*z* (NH_3 d.c.i.) 300 (80%, M^+ + 18), 265 (79%), 109 (100%).

Further evidence for structure **10** was provided by heating the mixture of sulfones 2-methyl-1-(*p*-tolylsulfonyl)hepta-2,6-diene and **9** in 60% aqueous acetic acid at 100 °C for 100 h. The cooled reaction mixture was worked up according to the procedure of Method B, and analysed by 300 MHz ^{1}H NMR spectroscopy. The signals assigned to the [1,3]-rearranged sulfone were still present but the resonances due to cyclopentane **9** had been lost. In addition, however, signals at δ 1.15 (6 H, s) and 3.51 (1 H, m) were now present. These correspond with resonances assigned to the hydroxy-sulfone **10**.

3-(p-*Tolylsulfonyl*)*octa*-2,7-*diene* **14**.—Butyllithium (2.5 cm^3 of a 1.1 mol dm^{-3} solution in hexanes, 1.1 equiv.) was added to a stirred solution of 3-*p*-tolylsulfonylprop-1-ene (0.49 g, 2.5 mmol) in 1:1 THF–ether (25 cm^3) cooled to −20 °C. The resulting solution was stirred at −20 °C for 30 min then cooled to −70 °C and stirred for a further 20 min at this temperature. 5-Bromopent-1-ene (1.1 equiv.) was added and the solution was stirred at −70 °C for 3 h then allowed to warm to room temperature. Glacial acetic acid (2 cm^3) was added and the reaction mixture was worked up as in the general procedure for alkylation of allylic sulfones. The crude reaction product consisted of a mixture of the title sulfone **14** and its allylic isomer. The crude product was taken up in dichloromethane (20 cm^3) then triethylamine (0.5 g, 2 equiv.) was added and the mixture was heated under reflux for 15 h. After cooling the solution was washed with dilute hydrochloric acid, water and brine, dried ($MgSO_4$) and the solvent removed under reduced pressure to give the crude sulfone as an oil. Chromatography on silica gel using 4:1 light petroleum–ether as eluent gave the sulfone **14** (0.24 g, 37%) as needles, m.p. 22–23 °C (from pentane); $\delta_H(CDCl_3)$ 1.40–1.53 (2 H, m, 5-H), 1.85 (3 H, d, *J* 7, 2-Me), 1.95–2.07 (2 H, m, 6-H), 2.24 (2 H, br t, *J* 9, 4-H), 2.46 (3 H, s, Me-C_6H_4-), 4.92–5.05 (2 H, m, 8-H), 5.72 (1 H, m, 7-H), 5.98 (1 H, q, *J* 7, 2-H), 7.32 (2 H, d, *J* 8, Ar) and 7.73 (2 H, d, *J* 8, Ar); ν_{max}(liq. film)/cm^{-1} 2925, 1640 (C=C), 1598 (Ar), 1310 and 1145 (SO_2); *m*/*z* (NH_3 d.c.i.) 282 (65%, M^+ + 18), 265 (100%, M^+ + 1), 139 (27%, $ArSO^+$) and 109 (55%, M+ − $ArSO_2$).

1-*Ethylidene*-2-(p-*tolylsulfonylmethyl*)*cyclopentane* **17**.—The reaction conditions used to prepare the sulfone **17** are outlined in Table 2.

The crude product from reaction 3, Table 2, was found to be a mixture of the cyclopentane **17** and toluene-*p*-thiosulfonate. This mixture was taken up in ethanol and treated with potassium toluene-*p*-thiolate. After work up and removal of solvent the residue was chromatographed on silica gel using 4:1 light petroleum–ether as eluent to give the sulfone **17** (72%) as a 20:1 mixture of diastereoisomers (after crystallisation) as needles, m.p. 58.5–60 °C (from pentane); $\delta_H(CDCl_3)$ 1.42–1.88 (4 H, m, 3-H and 4-H), 1.60 (3 H, d, *J* 7, C=C-Me), 2.03–2.28 (2 H, m, 5-H), 2.45 (3 H, s, Me-C_6H_4-), 2.70–2.85 (1 H, m, 2-H), 3.02 (1 H, dd, *J* 10, 15, -SO_2-CH_AH_B-), 3.32 (1 H, dd, *J* 4, 15, -$SO_2CH_AH_B$-), 5.17 (1 H, m, C=CH, major isomer), 5.32 (1 H, m, C=CH, minor isomer), 7.37 (2 H, d, *J* 8, Ar) and 7.80 (2 H, d, *J* 8, Ar); $\nu_{max}(CCl_4)/cm^{-1}$ 2930 (CH), 1598 (Ar), 1320 and 1150 (SO_2); *m*/*z* (NH_3 d.c.i.) 282 (100%, M^+ + 18), 265 (22%, M^+ + 1) and 109 (39%, M^+ − $ArSO_2$).

2-(p-*Tolylthiomethyl*)*cyclopentanone*.—A solution of titanium(IV) chloride (0.6 cm^3, 5.5 mol) in dry dichloromethane (5 cm^3) was added *via* syringe to a solution of chloro-*p*-

tolylthiomethane (7 mmol) and 1-trimethylsiloxycyclopentene (5 mmol) in dry dichloromethane (5 cm^3) cooled to −20 °C. The resulting orange solution was stirred at −20 °C for 1 h then poured into saturated aqueous sodium hydrogen carbonate. The mixture was extracted with ether (×5), the combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography of the residue on silica gel using 6:1 light petroleum–ether as eluent gave the keto sulfide as a clear oil (0.39 g, 35%); $\delta_H(CDCl_3)$ 1.67–2.25 (4 H, m, 3-H and 4-H), 2.28–2.43 (3 H, m, 2-H and 5-H), 2.35 (3 H, s, Me-C_6H_4), 2.75 (1 H, dd, *J* 10, 14, -SCH_AH_B-), 3.42 (1 H, dd, *J* 3, 14, -SCH_AH_B-), 7.12 (2 H, d, *J* 7, Ar) and 7.28 (2 H, d, *J* 7, Ar); $\nu_{max}(CCl_4)/cm^{-1}$ 2965 (CH) and 1740 (C=O).

2-(p-*Tolylsulfonylmethyl*)*cyclopentanone*.—(*a*) A solution of sulfone **17** (75 mg) in dry methanol (7 cm^3) was ozonolysed at −70 °C for 90 min until the solution was pale blue. Dimethyl sulfide (0.1 cm^3) was added and the solution was stirred with cooling for 2 h then was allowed to warm to room temperature overnight. The solvent was removed under reduced pressure and the residues were taken up in ether. The solution was washed with water and brine, dried $MgSO_4$ and the solvent removed under reduced pressure. The crude product was chromatographed on silica gel using 3:1 light petroleum–ethyl acetate as eluent to give the keto sulfone as an oil (18 mg); $\delta_H(CDCl_3)$ 1.60–2.18 (4 H, m, 3-H and 4-H), 2.30–2.47 (1 H, m, 2-H or 5-H), 2.45 (3 H, s, Me-C_6H_4-), 2.52–2.67 (2 H, m, 2-H or 5-H), 2.92 (1 H, dd, *J* 10, 15, -$SO_2CH_AH_B$-), 3.65 (1 H, dd, *J* 3, 15, -$SO_2CH_AH_B$-), 7.37 (2 H, d, *J* 8, Ar) and 7.80 (2 H, d, *J* 8, Ar); ν_{max}(liq. film)/cm^{-1} 1740 (C=O), 1598 (Ar), 1320 and 1145 (SO_2); *m*/*z* (NH_3 d.c.i.) 270 (100%, $M^+ + 18$), 253 (94%, $M^+ + 1$), 139 (30%, $ArSO^+$) and 97 (35%, $M^+ - ArSO_2$).

(*b*) Oxone (0.72 g, 3 equiv.) was added to a stirred solution of 2-(*p*-tolylthiomethyl)cyclopentanone (0.16 g, 0.78 mmol) in 1:1 water–methanol (8 cm^3) at 0 °C. The resulting slurry was stirred at 20 °C for 4 h then diluted with water and extracted with chloroform (×3). The combined organic extracts were washed with water, dried ($MgSO_4$) and solvent was removed under reduced pressure to give the crude sulfone as an oil. The product was dissolved in ether and filtered through a plug of silica gel. Evaporation of the solvent under reduced pressure gave the keto sulfone (0.152 g, 83%) as needles 79.5–81 °C from dichloromethane–pentane). This material was identical by TLC, 300 MHz ^1H NMR and IR spectroscopy to that obtained under (*a*) above.

1-p-*Tolylthio*-1-*trimethylsilylhex*-5-*ene*.—Methyllithium (2.3 cm^3 of a 0.9 mol dm^{-3} solution in hexane, 2.1 mmol) was added to a stirred solution of *p*-tolylthiotrimethylsilylmethane (0.4 g, 1.9 mmol) and TMEDA (0.4 cm^3, 2.6 mmol) cooled to 0 °C. The resulting solution was stirred at this temperature for 90 min then 1-bromopent-5-ene (0.25 cm^3, 2.1 mmol) was added and the mixture was stirred for a further 3 h at 0 °C. Saturated aqueous ammonium chloride was added and the mixture was extracted with light petroleum (×2). The organic extracts were washed with dilute hydrochloric acid (×2), dilute aqueous sodium hydrogen carbonate (×2) and brine. The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure to give the crude silyl sulfide as an oil. The product was dissolved in ether and filtered through a plug of silica gel. Evaporation of the solvent under reduced pressure gave the silyl sulfide (0.45 g, 85%) as a clear oil; $\delta_H(CDCl_3)$ 0.18 (9 H, s, $SiMe_3$), 1.48–1.83 (4 H, m, 2-H and 3-H) 1.93–2.07 (2 H, m, 4-H), 2.33 (3 H, s, Me-C_6H_4-), 2.43 (1 H, t, *J* 5, 1-H), 4.88–5.03 (2 H, m, 6-H), 5.68–5.85 (1 H, m, 5-H), 7.09 (2 H, d, *J* 8, Ar) and 7.28 (2 H, d, *J* 8, Ar); $\nu_{max}(CHCl_3)/cm^{-1}$ 3075, 2920 (CH), 1640 (C=C) and 840 (C-Si); *m*/*z* (NH_3 c.i.) 279 (100%, $M^+ + 1$) and 91 (82%, Ar^+).

1-p-*Tolylsulfonyl*-1-*trimethylsilylhex*-5-*ene*.—Hydrogen peroxide (0.1 cm^3 of a 100 vol, 30% solution, 2.2 equiv.) was added to a stirred solution of the above silyl sulfide (0.17 g) and sodium acetate (0.25 g, 5 equiv.) in glacial acetic acid (10 cm^3) heated to 50 °C. The reaction mixture was maintained at this temperature for 15 h then cooled and concentrated under reduced pressure. Water was added and the mixture was extracted with ether (×2). The ether extracts were washed with dilute sodium hydroxide solution until neutral, water and brine. The organic layer was dried ($MgSO_4$) and solvent was removed under reduced pressure to give the crude product. This material was dissolved in ether and filtered through a plug of silica gel. Evaporation of the solvent under reduced pressure gave the silyl sulfone (0.06 g, 30%) as a clear oil; $\delta_H(CDCl_3)$ 0.30 (9 H, s, -$SiMe_3$), 1.17–1.37 (2 H, m, 4-H), 2.45 (3 H, s, Me-C_6H_4-), 2.53 (1 H, t, *J* 5, 1-H), 4.77–4.90 (2 H, m, 6-H), 5.45–5.61 (1 H, m, 5-H), 7.32 (2 H, d, *J* 8, Ar) and 7.72 (2 H, d, *J* 8, Ar); ν_{max}(liq. film)/cm^{-1} 1640 (C=C), 1598 (Ar) 1300, 1140 (SO_2) and 845 (C-Si).

1-*Phenyl*-2-(p-*tolylsulfonyl*)*hepta*-1,6-*diene* **15**.—Butyllithium (0.15 cm^3 of a 1.5 mol dm^{-3} solution in hexane, 1.2 equiv.) was added to a stirred solution of the above silyl sulfone (0.056 g, 0.18 mmol) in THF (10 cm^3) cooled to −70 °C. The solution was allowed to warm slowly to −20 °C then re-cooled to −70 °C and excess fresh distilled benzaldehyde was added. The resulting mixture was warmed to 50 °C under vacuum (0.05 mmHg) to remove excess benzaldehyde. The product was purified by PLC to give vinyl sulfone **15** (30 mg, 50%) as a mixture of diastereoisomers; $\delta_H(CDCl_3)$ 1.53–1.88 (2 H, m, 4-H), 2.03 (2 H, m, 5-H, minor isomer), 2.18 (2 H, m, 5-H major isomer), 2.35 (3 H, s, Me-C_6H_4- major isomer), 2.47 (3 H, s, Me-C_6H_4-, minor isomer), 2.48 (2 H, t, *J* 8, 3-H minor isomer), 2.58 (2 H, t, *J* 8, major isomer), 4.90–5.12 (2 H, m, 7-H), 5.62–5.92 (1 H, m, 6-H), 7.02 (1 H, s, 1-H major isomer), 7.05–7.45 (8 H, m, 1-H minor isomer, Ph- and 2 ArH) and 7.60 (2 H, d, *J* 8, Ar); *m*/*z* (NH_3 d.c.i.) 344 (100%, $M^+ + 18$), 327 (45%, $M^+ + 1$), 171 (38%, $M^+ - ArSO_2$) and 170 (44%).

1-*Benzylidene*-2-(p-*tolylsulfonylmethyl*)*cyclopentane* **18**.—Cyclopentane **18** was prepared (General Method B) by treating vinyl sulfone **15** (33 mg) with sodium toluene-*p*-sulfinate (8 equiv.) in aqueous acetic acid at 100 °C for 20 h. The crude product was purified by chromatography on silica gel using 3:1 light petroleum–ether as eluent to give cyclopentane **18** (13 mg, 39%) as an oil; $\delta_H(CDCl_3)$ 1.53–2.22 (4 H, m, 3-H and 4-H), 2.48 (3 H, s, Me-C_6H_4-) 2.50–2.68 (2 H, m, 5-H), 3.02–3.13 (1 H, m, 2-H), 3.18 (1 H, dd, *J* 10, 14, -$SO_2CH_AH_B$-), 3.45 (1 H, dd, *J* 2.5, 14, -$SO_2CH_AH_B$-), 6.18 (1 H, br s, -CH=C), 7.15–7.37 (5 H, m, Ph-), 7.40 (2 H, d, *J* 8, Ar) and 7.85 (2 H, d, *J* 8, Ar).

1-p-*Tolylsulfonylocta*-1,7-*diene* **19**.—The sulfone **19** was prepared by the method of Inomata[12] from octa-1,7-diene (0.715 g), sodium toluene-*p*-sulfinate (1.5 equiv.) and iodine (1 equiv.). The crude product was dissolved in ether and filtered through a plug of silica gel. Removal of solvent under reduced pressure gave sulfone **19** (0.737 g, 43%) as a 9:2 mixture of *E*:*Z* isomers as an oil; $\delta_H(CDCl_3)$ 1.35–1.58 (4 H, m, 4-H and 5-H), 2.00–2.12 (2 H, m, 6-H), 2.20–2.32 (2 H, m, 3-H, *E*-isomer), 2.45 (3 H, s, Me-C_6H_4-), 2.62–2.73 (2 H, m, 3-H, *Z*-isomer), 4.90–5.08 (2 H, m, 8-H), 5.70–5.87 (1 H, m, 7-H), 6.20–6.38 (2 H, m, 1-H and 2-H, *Z*-isomer), 6.35 (1 H, br d, *J* 16, 1-H, *E*-isomer), 6.94 (1 H, dt, *J* 16, 7, 2-H, *E*-isomer), 7.53 (2 H, d, *J* 8, Ar), 7.76 (2 H, d, *J* 8, Ar, *E*-isomer) and 7.80 (2 H, d, *J* 8, Ar, *Z*-isomer); ν_{max}(liq. film)/cm^{-1} 2930 (CH), 1596 (Ar), 1319, 1150 (SO_2) and 1087; *m*/*z* (NH_3 c.i.) 282 (100%, $M^+ + 18$).

1-p-*Tolylsulfonylhexa*-1,5-*diene* **20**.—Sulfone **20** was prepared

as above from hexa-1,5-diene (0.64 g), sodium toluene-*p*-sulfinate and iodine as a 1:4 mixture of *Z*:*E* isomers (0.87 g, 47%) as an oil; $\delta_H(CDCl_3)$ 2.10–2.28 (2 H, m, 4-H), 2.29–2.40 (2 H, m, 3-H, *E*-isomer), 2.73–2.85 (2 H, m, 3-H, *Z*-isomer), 2.45 (3 H, s, Me-C_6H_4-), 4.94–5.10 (2 H, m, 6-H), 5.65–5.84 (1 H, m, 5-H), 6.15–6.40 (2 H, m, 1-H and 2-H, *Z*-isomer and 1 H, m, 1-H, *E*-isomer), 6.95 (1 H, dt, *J* 15, 6, 2-H, *E*-isomer), 7.33 (2 H, d, *J* 8, Ar), 7.75 (2 H, d, *J* 8, Ar, *Z*-isomer) and 7.80 (2 H, d, *J* 8, Ar, *E*-isomer); ν_{max}(liq. film)/cm^{-1} 2920 (CH), 1598 (Ar), 1302, 1145 (SO_2) and 1085; *m*/*z* (NH_3 a.c.e.) 254 (100%, $M^+ + 18$), 237 (51%, $M^+ + 1$), 139 (21%, $ArSO^+$) and 81 (28%, $M^+ - ArSO_2$).

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