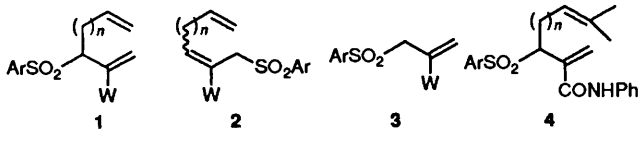
Radical Induced Cyclisations of Unsaturated Allylic Sulfones Containing an Activating Electron Withdrawing Group

Iain W. Harvey and Gordon H. Whitham*
Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, UK

Radical induced cyclisations of some unsaturated allylic sulfones containing an electron withdrawing amide group β-to the sulfone group are described. Products containing five-, six- and seven-membered rings have been obtained using appropriate precursors. In the case of the six-membered ring, examples of all four possible modes of cyclisation were found: *i.e. exo*-6-*exo*, *exo*-6-*endo*, *endo*-6-*exo* and *endo*-6-*endo*.

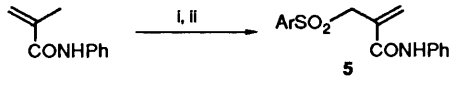
The previous paper[1] was concerned with attempts to extend the scope of radical induced cyclisation of unsaturated sulfones beyond that of the *exo*-5-*exo*-mode, which in our earlier work[2] had proved to be quite widely applicable. In fact only modest extensions were achieved, and we described examples of the *endo*-5-*exo*- and *exo*-5-*exo*-*ipso*-cyclisations. It was argued that the introduction of an electron withdrawing group onto the β-position of the allylic sulfone might facilitate the cyclisation step owing to the well known favourable influence of a β-electron withdrawing group on rates of addition of nucleophilic alkyl radicals to alkenes.[3] The present paper describes the results of our investigations into this possibility.

For the planned investigation a general procedure was required for the preparation of a series of allylic sulfones of general type **1** and their allylic isomers **2**, where W is a generalised electron withdrawing group. Compounds **1** should be accessible by alkylation of the simpler allylic sulfone **3** provided that the alkylation procedure used is compatible with the W group. Preliminary investigations showed that attempts at deprotonation–alkylation using compounds **3** (W = CO_2Me, CO_2H, CN, or SO_2Ar) failed, either because the bases used reacted with the functional group or because substitution by addition–elimination occurred. Fortunately, as was already known,[4] allylic sulfone amides with a free NH undergo deprotonation–monoalkylation provided two equivalents of butyllithium are used, one equivalent to deprotonate the amide NH, thereby protecting the amide function from further attack, and the second equivalent to deprotonate α- to the sulfone group.



1 **2** **3** **4**

The required allylic sulfone amide **5** was readily obtained by the two step sequence shown in Scheme 1. Related preparations of functionalised vinyl and allyl sulfones have been described by other workers.[5]



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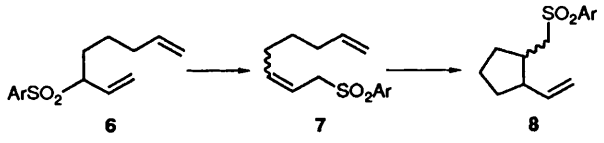
Scheme 1 *Reagents:* i, *p*-TsI–CCl_4, *hν*; ii, Et_3N–CH_2Cl_2, reflux

Alkylated sulfone amides **1** (W = CONHPh, n = 2, 3, 4 and 6) and **4** (n = 1, 2 and 3) were then prepared, in acceptable yields, by treatment of the parent sulfone amide **5** with 2.1 equivalents of butyllithium in the presence of 2 equivalents of hexamethylphosphoramide (HMPA) in THF at −70 °C, followed by alkylation with the appropriate alkenyl halide. As will be seen later, it transpired that allylic rearrangement of sulfones **1** (W = CONHPh) under radical conditions occurred only sluggishly, and it turned out to be more convenient to make the rearranged sulfones **2** (W = CONHPh, n = 2 and 3) by treatment of the appropriate precursors **1** with sodium toluene-*p*-sulfinate (NaTs) in aqueous DMSO. Under these conditions, it seems likely that rearrangement occurs by nucleophilic addition–elimination of toluene-*p*-sulfinate ion facilitated by the presence of the electron withdrawing amide group.

In our previous investigations[2] on the radical catalysed rearrangement–cyclisation of unsaturated allylic sulfones the prototypical example was that shown in Scheme 2, where initial

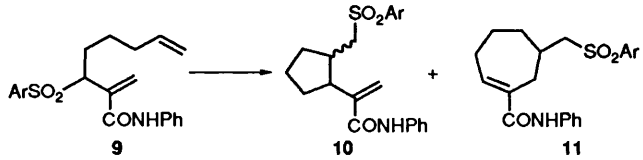


6 **7** **8**

Scheme 2

1,3-rearrangement of sulfone **6** to its allylic isomer **7** was followed by *exo*-5-*exo*-cyclisation to the vinyl cyclopentane **8**. It was therefore of interest to examine the behaviour of the related compound **9** in the amide-activated series.

Cyclisation of amide sulfone **9** was attempted under the standard conditions, namely heating with NaTs in aqueous acetic acid.[1,2] Two products were formed, the minor one being the cyclopentane derivative **10**, analogous to the formation of **8** in Scheme 2, while the major, isomeric, product was shown to be the cycloheptene derivative **11**, Scheme 3. Key features in the

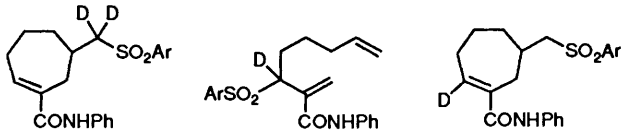


9 **10** **11**

Scheme 3

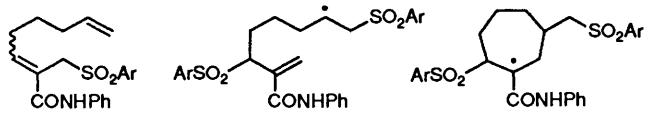
NMR spectrum, helping to identify **11**, were signals in the region of δ 3 characteristic of the diastereotopic hydrogens α-to sulfone and a low field triplet at δ 7.18 attributable to the alkene hydrogen. Further confirmation of structure **11** was provided by deuteriation studies. Treatment of **11** with NaOD–D_2O gave the labelled sulfone **12** which had a ^1H NMR spectrum similar to that of **11** but without the signals in the δ 3 region. Furthermore the deuteriated sulfone **13**, obtained by deuteriation of sulfone amide **9**, gave, on cyclisation, the deuteriated cycloheptene **14** which had a ^1H NMR spectrum

similar to that for **11** apart from the absence of the resonance at δ 7.18. The ratio of **11** to **10** formed in the cyclisation varied somewhat from run to run, but **11** was always the major product and in a typical experiment respective yields were **10**, 15% and **11**, 70%. Clearly, in comparison to the unsubstituted system, the presence of the electron withdrawing amide group has led to a marked preference for direct *exo*-7-*endo*-cyclisation.



12 **13** **14**

In comparing the two systems, *i.e.* Scheme 3 *vs.* Scheme 2, addition of the electrophilic arenesulfonyl radical to the electron deficient double bond in **9** should be disfavoured, thereby lowering the rate of radical promoted 1,3-rearrangement to the allylic isomer **15**, which is the precursor of the cyclopentane **10**. However sulfonyl radical addition to the distal double bond is not affected, and the intermediate radical **16** so formed, being a nucleophilic alkyl radical, adds efficiently to the double bond of the α,β-unsaturated amide leading, *via* the adduct radical **17**, to the cycloheptene **11**.

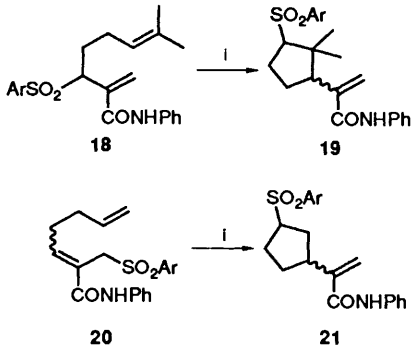


15 **16** **17**

The role of isomer **15** in the formation of cyclopentane **10** was confirmed by a separate preparation of **15**, as described earlier, and its subjection to the NaTs–aq. AcOH reaction conditions. The only cyclic product isolated was now the compound **10**, obtained in 73% yield by the *exo*-5-*exo*-process. Thus the starting material **9** can be converted selectively into either the cycloheptene **11** or the cyclopentane **10** by appropriate choice of reagents and conditions.

To explore further the scope of the amide-activated cyclisation, we examined the behaviour of the acyclic amide sulfones, prepared as described earlier, under the standard NaTs–aq. AcOH conditions. The intention was to cover fairly systematically the various cyclisation modes for different ring sizes.

For 5-ring formation, in addition to the *exo*-5-*exo* process already discussed, two examples of *endo*-5-*exo* cyclisation were found, Scheme 4. In the first of these, **18** was converted into **19**

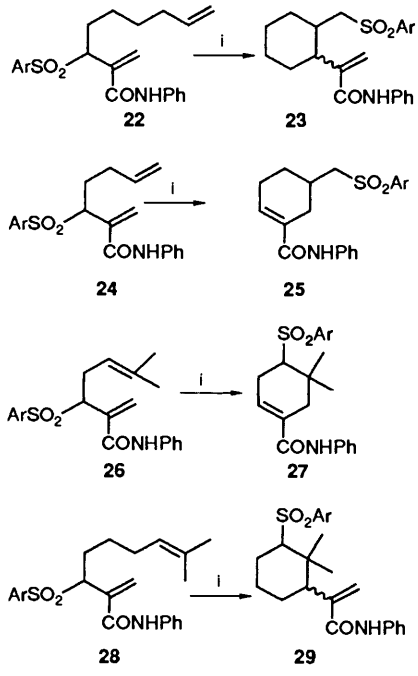


18 **19** **20** **21**

Scheme 4 *Reagents and conditions:* i, NaTs–aq. AcOH, 100 °C

in 83% yield. The trisubstituted nature of the isolated double bond in **18** favours initial *endo*-attack of $ArSO_2^{\bullet}$, but in contrast to the efficient 7-*endo*-cyclisation of **16**, attack on the double bond of the unrearranged allylic sulfone is slow, presumably because the relevant radical is trisubstituted. Thus sulfone 1,3-rearrangement has time to occur, and it is the rearranged isomer which undergoes 5-*exo*-cyclisation to give **19**. In the second example, the 1,3-rearranged sulfone **20** had to be prepared first before it was subjected to cyclisation conditions giving the cyclopentane **21** (50%). Not surprisingly, the formally possible *exo*-4-*exo*-cyclisation does not occur and **21** is formed *via* the primary radical obtained from attack of $ArSO_2^{\bullet}$ at the substituted end of the isolated double bond of **20**.

For 6-membered ring formation, examples of all four possible modes of cyclisation were found (Scheme 5). The *exo*-*exo*-



22 **23** **24** **25** **26** **27** **28** **29**

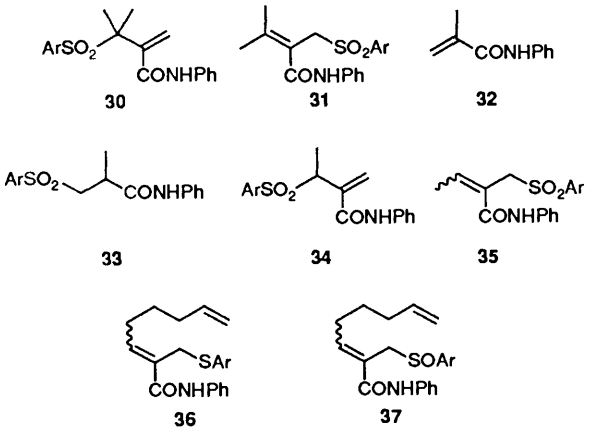
Scheme 5 *Reagents and conditions:* i, NaTs–aq. AcOH, 100 °C

process involving precursor **22**, giving **23** in 77% yield, must involve prior 1,3-rearrangement before cyclisation. Clearly *exo*-8-*endo*-cyclisation does not compete. The *exo*-6-*endo*-cyclisation of **24** to **25** (82% yield) is noteworthy in that cyclisation has occurred faster than 1,3-rearrangement of the allylic sulfone. Had such rearrangement occurred to any significant extent, to give **20**, the latter would have been converted into sulfone **21**, as shown earlier. Less efficient were the *endo*-6-*endo*-cyclisation of **26** into **27** (20%), and the *endo*-6-*exo*-cyclisation involved in the second step of the conversion of **28** into **29** (25%). In the former case, cyclisation involves attack of a tertiary radical on the double bond of the allylic sulfone, a relatively inefficient process, and 1,3-rearranged sulfone, which has no further fruitful reaction pathway open to it, is also formed. In the second case, formation of **29**, the low yield may reflect attack of a tertiary radical on the allylic double bond after 1,3-rearrangement but since no other characterisable materials were isolated, further discussion is unwarranted.

One of the considerations in the above discussions was that allylic sulfones substituted at the 2-position with an amide group would only rearrange slowly under radical conditions. This was confirmed in the case of the amide sulfone **30** (obtained by methylation of sulfone **5**) by showing that rearrangement to **31** was slow using benzoyl peroxide in CCl_4 under reflux (incomplete after 30 h). Under similar conditions 3-methyl-3-*p*-tolylsulfonylbut-1-ene undergoes complete 1,3-rearrangement in 1 h.[6]

It is known that addition of sulfinic acids to certain α,β-unsaturated carbonyl compounds can occur on treatment with

the appropriate sodium sulfinate in a protic solvent.[7] We observed such addition in a number of simple cases on treatment under our NaTs–aq. AcOH conditions.[8] For example, the α,β-unsaturated amide **32** gave the adduct **33**. However the substituted sulfone amide **34** was converted into the 1,3-rearranged isomer **35** on similar treatment. Apparently the position of equilibrium for such additions is highly sensitive to structural changes in the substrate, and for fairly heavily substituted cases such as **34**, **35**, and the products from our cyclisation reactions, equilibrium favours the α,β-unsaturated amide rather than the adduct.



Given the availability of the amide sulfone **9**, and its susceptibility, as already seen, to substitution reactions of the S_N2' type, the opportunity was taken of preparing amide sulfide **36** by treatment of **9** with sodium toluene-*p*-thiolate in methanol. The analogous sulfoxide **37** was obtained by oxidation of **36** with hydrogen peroxide. Compounds **36** and **37** were of interest as analogues of sulfone **15** since they might undergo radical initiated cyclisation by analogy to the cyclisation of **15** to **10**. However, treatment of sulfide **36** with either benzoyl peroxide in cyclohexane or toluene-*p*-thiol and benzoyl peroxide in CCl_4 gave recovered starting material. Similarly prolonged heating of sulfoxide **37** with benzoyl peroxide in *tert*-butanol led to recovery of unchanged starting material. Apparently cyclisation of **36** or **37** is a less facile process than the analogous reaction for sulfone **15**.

Experimental

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

N-Phenyl-2-(p-tolylsulfonylmethyl)propenamide **5**.—A saturated solution of iodine (17.5 g) in ethanol was added dropwise to a stirred solution of sodium toluene-*p*-sulfinate in water (1 dm^3) in the dark. The yellow precipitate was collected, washed with water then dissolved in benzene and the solution dried ($MgSO_4$). *N*-Phenyl methacrylamide[9] (7.7 g) was added and the solution was stirred in daylight at 20 °C until no starting material was detected by TLC. Solvent was removed under reduced pressure and the residue was taken up in dichloromethane and heated at reflux for 15 h in the presence of triethylamine (40 g). The solution was cooled, washed with dilute hydrochloric acid and water, dried ($MgSO_4$) and solvent was removed under reduced pressure to give the crude sulfone. Filtration of a solution of the crude sulfone in dichloromethane through a plug of silica gel followed by removal of the solvent under reduced pressure gave the *sulfone* **5** (12.3 g, 81%) as needles, m.p. 168.5–169.5 °C (from ethanol) (Found: C, 64.6; H, 5.55; N, 4.35. $C_{17}H_{17}NO_3S$ requires C, 64.75; H, 5.45; N, 4.45%); $\delta_H(CDCl_3)$ 2.40 (3 H, s, Me-C_6H_4-), 4.22 (2 H, s, -SO_2CH_2-), 5.59 (1 H, s, 3-H), 6.17 (1 H, s, 3-H), 7.14 (1 H, t, *J* 8, Ph), 7.29–7.38 (4 H, m, Ph and Ar), 7.50 (2 H, d, *J* 8, Ph), 7.78 (2 H, d, *J* 8, Ar) and 8.34 (1 H, br s, NH); $\nu_{max}(CDCl_3)/cm^{-1}$ 3425, 3325 (NH), 1680 (C=O), 1598 (Ar), 1320 and 1145 (SO_2); *m/z* (NH_3 d.c.i.) 316 (100%, $M^+ + 1$) and 160 (36%, $M^+ - ArSO_2$).

General Procedure for the Monoalkylation of N-Phenyl-2-(p-tolylsulfonylmethyl)propenamide **5**.—Butyllithium (2.1 equiv.) was added dropwise *via* syringe to a stirred solution of sulfone **5** in dry THF cooled to −70 °C. Dry HMPA (2.0 equiv.) was then added and the resulting solution was maintained at −70 °C for 1 h. The alkyl halide (1.1 equiv.) was added and the mixture was stirred at −70 °C for 3 h then allowed to warm slowly to −20 °C (bath temperature). Glacial acetic acid (0.5 cm^3/mmol of sulfone) was added and then the resulting mixture was partitioned between water and ether. The organic layer was washed with dilute sodium hydroxide solution, dilute aqueous sodium bisulfite, dilute hydrochloric acid, water and brine. After drying ($MgSO_4$), the solvent was removed under reduced pressure to give the crude alkylated sulfones as oils.

The following compounds were prepared by this method:

2-Methylene-N-phenyl-3-(p-tolylsulfonyl)hept-6-enamide **24**.—The sulfone **24** was prepared from sulfone **5** (0.95 g) and 4-bromobut-1-ene (0.35 cm^3) as needles, m.p. 130.5–131.5 °C (from pentane–chloroform) (0.42 g, 39%) after chromatography on silica gel using 4:1 light petroleum–ethyl acetate as eluent; $\delta_H(CDCl_3)$ 1.93–2.30 (4 H, m, 4-H and 5-H), 2.38 (3 H, s, Me-C_6H_4-), 4.40 (1 H, dd, *J* 3, 11, 3-H), 4.97–5.01 (2 H, m, 7-H), 5.63–5.80 (1 H, m, 6-H), 5.67 (1 H, s, C=CH_2), 6.17 (1 H, s, C=CH_2), 7.13 (1 H, t, *J* 7, Ph), 7.29–7.38 (3 H, m, Ph and Ar), 7.48 (2 H, d, *J* 8, Ph), 7.77 (2 H, d, *J* 8, Ar) and 8.13 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3320 (NH), 1670 (C=O), 1599 (Ar), 1315 and 1145 (SO_2); *m/z* (NH_3 d.c.i.) 370 (100%, $M^+ + 1$), 216 (70%), 214 (48%, $M^+ - ArSO_2$) and 91 (26%, Ar).

2-Methylene-N-phenyl-3-(p-tolylsulfonyl)oct-7-enamide **9**. The *sulfone* **9** was prepared from sulfone **5** (0.95 g) and 5-bromopent-1-ene (0.4 cm^3) as needles, m.p. 76.5–78 °C (from pentane–chloroform) (0.71 g, 62%) after chromatography on silica gel using 4:1 light petroleum–ethyl acetate as eluent (Found: C, 68.8; H, 6.7; N, 3.5. $C_{22}H_{25}NO_3S$ requires C, 68.9; H, 6.55; N, 3.65%); $\delta_H(CDCl_3)$ 1.29–1.48 (2 H, m, 5-H), 1.82–2.20 (4 H, m, 4-H and 6-H), 2.37 (3 H, s, Me-C_6H_4-), 4.40 (1 H, dd, *J* 3, 12, 3-H) [absent in the ^{1}H NMR spectrum of 3-deuterio-2-methylene-*N*-phenyl-3-(*p*-tolylsulfonyl)oct-7-enamide **13**], 4.88–5.02 (2 H, m, 8-H), 5.65–5.86 (1 H, m, 7-H), 5.67 (1 H, s, C=CH_2), 6.13 (1 H, s, C=CH_2), 7.13 (1 H, t, *J* 7, Ph), 7.28–7.38 (4 H, m, Ph and Ar), 7.48 (2 H, d, *J* 7, Ph), 7.77 (2 H, d, *J* 8, Ar) and 8.08 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3320 (NH), 1678 (C=O), 1600 (Ar), 1305 and 1445 (SO_2); *m/z* (NH_3 d.c.i.) 384 (88%, $M^+ + 1$), 230 (56%), 228 (100%, $M^+ - ArSO_2$), 139 (38%, $ArSO^+$), 94 (38%) and 91 (42%, Ar^+).

2-Methylene-N-phenyl-3-(p-tolylsulfonyl)non-8-enamide **22**.—The sulfone **22** was prepared from sulfone **5** (0.95 g) and 6-bromohex-1-ene (0.45 cm^3) as needles, m.p. 72.5–74 °C (from pentane–chloroform) (0.5 g, 43%) after chromatography on silica gel using 4:1 light petroleum–ethyl acetate as eluent; $\delta_H(CDCl_3)$ 1.29–1.44 (4 H, m, 5-H and 6-H), 1.88–2.12 (4 H, m, 4-H and 7-H), 2.35 (3 H, s, Me-C_6H_4-), 4.43 (1 H, dd, *J* 3.8, 11.6, 3-H), 4.88–4.97 (2 H, m, 9-H), 5.65–5.79 (1 H, m, 8-H), 5.68 (1 H, s, C=CH_2), 6.15 (1 H, s, C=CH_2), 7.09 (1 H, t, *J* 7.3, Ph), 7.27–7.33 (4 H, m, Ph and Ar), 7.47 (2 H, d, *J* 8.6, Ph), 7.75 (2 H, d, *J* 8.3, Ar) and 8.18 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3320 (NH), 1678 (C=O), 1599 (Ar), 1315 and 1148 (SO_2); *m/z*

Table 1 Products from cyclisation of the unsaturated sulfone amides

Entry	Substrate	Time (h)	Product(s) (yield %)
1	**9**	15	**11** (70) + **10** (15)
2	**13**	15	**14** (58) + 2′-deuterio-**10** (22)
3	**15**	16	**10** (73)
4	**22**	20	**23** (77)
5	**24**	20	**25** (82)
6	**20**	20	**21** (50)[a]
7	**26**	20	**27** (20) + 1,3-rearranged **26** (16)
8	**18**	20	**19** (83)
9	**28**	19	**29** (25)[b]

[a] As a 3:1 mixture of diastereoisomers. [b] Only one diastereoisomer isolated, considered to be the *cis*-isomer; other uncharacterised products also formed.

(NH_3 d.c.i.) 398 (77%, $M^+ + 1$), 242 (100%, $M^+ - ArSO_2$), 139 (52%, $ArSO^+$) 93 (44%, $PhNH_2^+$) and 91 (39%, Ar^+).

6-*Methyl*-2-*methylene*-N-*phenyl*-3-(p-*tolylsulfonyl*)*hept*-5-*enamide* **26**. The *sulfone* **26** was prepared from sulfone **5** and prenyl bromide, as needles, m.p. 104–106 °C (from pentane–chloroform) (87%) after chromatography on silica gel using 3:1 light petroleum–ethyl acetate as eluent (Found: C, 69.05; H, 6.6; N, 3.6. $C_{22}H_{25}NO_3S$ requires C, 68.9; H, 6.55; N, 3.65%); $\delta_H(CDCl_3)$ 1.55 (3 H, s, 6-Me), 1.61 (3 H, s, 6-Me), 2.37 (3 H, s, Me-C_6H_4-), 2.57–2.68 (1 H, m, 4-H), 2.76–2.86 (1 H, m, 4-H), 4.45 (1 H, dd, *J* 4.5, 6.7, 3-H), 4.92 (1 H, br t, *J* 7, 5-H), 5.68 (1 H, s, C=CH_2), 6.15 (1 H, s, C=CH_2), 7.11 (1 H, t, *J* 7.4, Ph), 7.29–7.35 (4 H, m, Ph and Ar), 7.48 (2 H, d, *J* 8.2, Ph), 7.77 (2 H, d, *J* 8.2, Ar) and 8.17 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3420, 3320, (NH), 1675 (C=O), 1598 (Ar), 1305 and 1150 (SO_2); *m*/*z* (NH_3 d.c.i.) 384 (100%, $M^+ + 1$) and 228 (70%, $M^+ - ArSO_2$).

7-*Methyl*-2-*methylene*-N-*phenyl*-3-(p-*tolylsulfonyl*)*oct*-6-*enamide* **18**. The *sulfone* **18** was prepared from sulfone **5** (0.95 g) and 1-iodo-4-methylpent-3-ene[10] (0.7 g) as needles, m.p. 73–75 °C (from pentane–chloroform) (0.64 g, 54%) after chromatography on silica gel using 4:1 light petroleum–ethyl acetate as eluent; $\delta_H(CDCl_3)$ 1.52 (3 H, s, 7-Me), 1.63 (3 H, s, 7-Me), 1.83–2.22 (4 H, m, 4-H and 5-H), 2.38 (3 H, s, Me-C_6H_4-), 4.37 (1 H, dd, *J* 3, 11, 3-H), 4.95–5.05 (1 H, br s, 6-H), 5.60 (1 H, s, C=CH_2), 6.19 (1 H, s, C=CH_2), 7.13 (1 H, t, *J* 7, Ph), 7.27–7.38 (4 H, m, Ph and Ar), 7.47 (2 H, d, *J* 9, Ph), 7.73 (2 H, d, *J* 8, Ar) and 8.25 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3320 (NH), 1675 (C=O), 1598 (Ar), 1310 and 1145 (SO_2); *m*/*z* (NH_3 d.c.i.) 398 (50%, $M^+ + 1$), 244 (62%), 242 (100%, $M^+ - ArSO_2$) 93 (47%, $PhNH_2^+$) and 91 (41%, Ar^+).

8-*Methyl*-2-*methylene*-N-*phenyl*-3-(p-*tolylsulfonyl*)*non*-7-*enamide* **28**. The *sulfone* **28** was prepared from sulfone **5** (0.31 g) and 1-iodo-5-methylhex-4-ene[11] (0.25 g) as needles, m.p. 117–118.5 °C (from pentane–chloroform) (0.215 g, 52%) after chromatography on silica gel using 4:1 light petroleum–ethyl acetate as eluent (Found: C, 69.65; H, 7.3; N, 3.2. $C_{24}H_{29}NO_3S$ requires C, 70.05; H, 7.1; N, 3.4%); $\delta_H(CDCl_3)$ 1.27–1.45 (2 H, m, 5-H), 1.55 (3 H, s, 8-Me), 1.62 (3 H, s, 8-Me), 1.87–2.12 (4 H, m, 6-H and 4-H), 2.37 (3 H, s, Me-C_6H_4-), 4.40 (1 H, dd, *J* 3.8, 11.6, 3-H), 4.98 (1 H, br t, *J* 6, 7-H), 5.66 (1 H, s, C=CH_2), 6.15 (1 H, s, C=CH_2), 7.12 (1 H, t, *J* 7.3, Ph), 7.29–7.34 (4 H, m, Ph and Ar), 7.46 (2 H, d, *J* 8, Ph), 7.75 (2 H, d, *J* 8, Ar) and 8.14 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3415, 3320 (NH), 1678 (C=O), 1599 (Ar), 1315 and 1145 (SO_2); *m*/*z* (NH_3 d.c.i.) 412 (27%, $M^+ + 1$), 258 (100%) and 256 (38%, $M^+ - ArSO_2$).

General Procedure for [1.3]-*Rearrangement of the Alkyl-substituted Sulfone Amides*.—Sodium toluene-*p*-sulfinate (5 equiv.) was added to a stirred solution of the sulfone amide in DMSO (approx. 0.5 mol dm^{-3} in sulfone) and the mixture was heated at 75 °C for 3 h. A five-fold excess of water was added and the solution was extracted repeatedly with ether. The organic extracts were combined, washed with water and brine, dried ($MgSO_4$) and solvent removed under reduced pressure to give the rearranged sulfone amides.

The following compounds were prepared by this method:

3-*Methyl*-N-*phenyl*-2-(p-*tolylsulfonylmethyl*)*but*-2-*enamide* **31**. Treatment of 3-methyl-2-methylene-*N*-phenyl-3-(*p*-tolylsulfonyl)butanamide **30** with sodium toluene-*p*-sulfinate according to the general procedure gave the sulfone **31** (90%) as needles, m.p. 162–164 °C (from pentane–chloroform); δ_H-($CDCl_3$) 1.77 (3 H, s, 3-Me), 2.05 (3 H, s, 3-Me), 2.42 (3 H, s, Me-C_6H_4-), 4.15 (2 H, s, -SO_2CH_2-), 7.12 (1 H, t, *J* 7, Ph), 7.27–7.40 (4 H, m, Ph and Ar), 7.57 (2 H, d, *J* 7, Ph) and 7.77 (2 H, d, *J* 8, Ar); $\nu_{max}(CHCl_3)/cm^{-1}$ 3420, 3320 (NH), 1670 (C=O), 1600 (Ar), 1325 and 1145 (SO_2); *m*/*z* (NH_3 d.c.i.) 344 (83%, $M^+ + 1$), 343 (30%, M^+), 251 (77%, $M^+ - PhNH$), 188 (100%, $M^+ - ArSO_2$), 139 (64%, $ArSO^+$) and 91 (35%, Ar^+).

N-*Phenyl*-2-(p-*tolylsulfonylmethyl*)*hepta*-2,6-*dienamide* **20**. The reaction of 2-methylene-*N*-phenyl-3-(*p*-tolylsulfonyl)hept-6-enamide **24** with sodium toluene-*p*-sulfinate according to the general procedure gave the sulfone **20** (95%) as a 10:1 mixture of *E*:*Z* isomers; $\delta_H(CDCl_3)$ 2.08–2.24 (4 H, m, 4-H and 5-H), 2.40 (3 H, s, Me-C_6H_4-, *E*-isomer), 2.43 (3 H, s, Me-C_6H_4-, *Z*-isomer), 4.05 (2 H, s, -SO_2CH_2-, *Z*-isomer), 4.28 (2 H, s, -SO_2CH_2-, *E*-isomer), 4.99–5.10 (2 H, m, 7-H) 5.67–5.88 [1 H, m, 6-H (both isomers) and 1 H, m, 3-H, *Z*-isomer], 6.78 (1 H, br t, *J* 7.5, 3-H, *E*-isomer), 7.12 (1 H, t, *J* 6.5, Ph), 7.29–7.40 (4 H, m, Ph and Ar), 7.50 (2 H, br d, *J* 8, Ph, *E*-isomer), 7.57 (2 H, br d, *J* 8, Ph, *Z*-isomer), 7.78–7.85 (2 H, m, Ar) and 8.42 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3330 (NH), 1672 (C=O), 1598 (Ar), 1318 and 1142 (SO_2); *m*/*z* (NH_3 c.i.) 370 (53%, $M^+ + 1$), 263 (28%), 214 (100%, $M^+ - ArSO_2$) and 96 (32%).

N-*Phenyl*-2-(p-*tolylsulfonylmethyl*)*octa*-2,7-*dienamide* **15**. Treatment of 2-methylene-*N*-phenyl-3-(*p*-tolylsulfonyl)oct-7-enamide **9** with sodium toluene-*p*-sulfinate according to the general procedure gave the sulfone **15** (94%) as a 5:1 mixture of *E*:*Z* isomers; $\delta_H(CDCl_3)$ 1.42–1.60 (2 H, m, 5-H), 1.97–2.10 (4 H, m, 4-H and 6-H), 2.42 (3 H, s, Me-C_6H_4-, *E*-isomer), 2.44 (3 H, s, Me-C_6H_4-, *Z*-isomer), 4.09 (2 H, s, -SO_2CH_2-, *Z*-isomer) 4.27 (2 H, s, -SO_2CH_2-, *E*-isomer), 4.95–5.08 (2 H, m, 8-H), 5.67–5.88 [1 H, m, 7-H (both isomers) and 1 H, m, 3-H, *Z*-isomer], 6.80 (1 H, t, *J* 7, 3-H, *E*-isomer), 7.12 (1 H, t, *J* 7, Ph), 7.30–7.42 (4 H, m, Ph and Ar), 7.52 (2 H, d, *J* 7, Ph, *E*-isomer), 7.58 (2 H, d, *J* 7, Ph, *Z*-isomer), 7.80 (2 H, d, *J* 8, Ar) and 7.47 (1 H, br s, NH); *m*/*z* (NH_3 d.c.i.) 384 (100%, $M^+ + 1$), 228 (34%, $M^+ - ArSO_2$) and 139 (18%, $ArSO_2$).

Cyclisation of the Alkyl-substituted Sulfone Amides.—The cyclisation of the sulfone amides was carried out using the procedure described in the previous paper[1] (Method B). The results are summarised in Table 1. Data for the individual compounds are given below.

N-*Phenyl*-6-(p-*tolylsulfonylmethyl*)*cyclohept*-1-*enecarboxamide* **11**. The *sulfone* **11** was isolated as pale yellow needles, m.p. 171.5–173 °C (from pentane–chloroform) after chromatography on silica gel using 2:1 light petroleum–ethyl acetate as eluent (Found: C, 69.25; H, 6.75; N, 3.45. $C_{22}H_{25}NO_3S$ requires C, 68.9; H. 6.55; N, 3.65%); $\delta_H(CDCl_3)$ 1.38–1.98 (4 H, m, 4-H and 5-H), 2.20–2.45 (3 H, m, 3-H and 6-H), 2.46 (3 H, s, Me-C_6H_4-), 2.68 (1 H, dd, *J* 9, 16, 7-H), 2.98 (2 H, each d, *J* 16, 7-H and -SO_2CH_2), 3.23 (1 H, dd, *J* 9, 16, -SO_2CH_2), 7.11 (1 H, t, *J* 8, Ph), 7.18 (1 H, t, *J* 7, 2-H) (absent in the spectrum of the deuteriated sulfone **14**), 7.3–7.42 (4 H, m, Ph and Ar), 7.73–7.87 (4 H, m, Ph and Ar) and 8.73 (1 H, br s, NH); $\delta_C(CDCl_3)$ 21.50 (q), 23.83 (t), 27.89 (t), 31.10 (d), 32.95 (t), 39.10 (t), 61.01 (t), 119.96 (d), 123.76 (d), 127.67 (d), 128.71 (d), 130.02 (d), 136.40 (s), 137.22 (s), 138.81 (s), 141.64 (d), 144.96 (s) and 166.39 (s); $\nu_{max}(CHCl_3)/cm^{-1}$ 3355 (NH), 1670 (C=O), 1598 (Ar), 1315

and 1145 (SO_2); *m/z* (NH_3 d.c.i.) 384 (100%, $M^+ + 1$) and 230 (52%).

Deuteriation of N-*phenyl*-6-(p-*tolylsulfonylmethyl*)*cyclohept*-1-*enecarboxamide* **11**. Sodium (*ca.* 2 mg) was added to a mixture of sulfone **11** (5 mg) in deuterium oxide (2.5 cm^3) and the resulting solution was heated to reflux. After 1 h the mixture had become turbid and a further portion of deuterium oxide (1 cm^3) was added. The mixture was heated at reflux for a further 16 h. The cooled mixture was extracted into ether (×2) and the organic extracts were washed with dilute hydrochloric acid, water and brine. Drying ($MgSO_4$) and evaporation of the solvent under reduced pressure gave the crude sulfone. Column chromatography on silica gel using 2:1 light petroleum–ethyl acetate as eluent gave the deuteriated sulfone **12** (2 mg). The 300 MHz ^1H NMR spectrum was similar to that for the sulfone **11** but without a resonance at δ 3.23, and the signal at δ 2.98 was a simple doublet.

N-*Phenyl*-2-[2′-(p-*tolylsulfonylmethyl*)*cyclopentyl*]*propenamide* **10**. The *sulfone* **10** was obtained as a 3:2 mixture of diastereoisomers as needles, m.p. 166.5–168.5 °C (from pentane–chloroform) after chromatography on silica gel using 3:1 light petroleum–ethyl acetate as eluent (Found: C, 68.65; H, 6.65; N, 3.5. $C_{22}H_{25}NO_3S$ requires C, 68.9; H, 6.55; N, 3.65%); $\delta_H(CDCl_3)$ 1.38–2.17 (6 H, m, 3′-H, 4′-H and 5′-H), 2.37 (3 H, s, Me-C_6H_4-, major isomer), 2.43 (3 H, s, Me-C_6H_4-, minor isomer), 2.50–2.60 (1 H, br s, 2′-H), 2.92 (1 H, dd, *J* 9, 14, -SO_2CH_2-, major isomer), 3.05 (1 H, dd, *J* 9, 14, -SO_2CH_2-, minor isomer), 3.09–3.22 (1 H, m, 1′-H), 3.17 (1 H, dd, *J* 4, 14, -SO_2CH_2-, major isomer), 3.35 (1 H, dd, *J* 4, 14, -SO_2CH_2-, minor isomer) 5.35 (1 H, s, 3-H, major isomer), 5.37 (1 H, s, 3-H, minor isomer), 5.67 (1 H, s, 3-H, minor isomer) 5.78 (1 H, s, 3-H, major isomer), 7.13 (1 H, t, *J* 7, Ph), 7.17–7.37 (4 H, m, Ph and Ar), 7.52 (2 H, d, *J* 7, Ph, major isomer), 7.55 (2 H, d, *J* 7, Ph, minor isomer), 7.70 (2 H, d, *J* 8, Ar, major isomer), 7.76 (2 H, d, *J* 8, Ar minor isomer) and 7.78 (1 H, br s, NH); ν_{max}-($CHCl_3$)/cm^{-1} 3430, 3340 (NH), 1675 (C=O), 1599 (Ar), 1305 and 1150 (SO_2); *m/z* (NH_3 d.c.i.) 401 (42%, $M^+ + 18$), 384 (100%, $M^+ + 1$) and 230 (44%, $M^+ - ArSO_2$).

N-*Phenyl*-2-[2′-(p-*tolylsulfonylmethyl*)*cyclohexyl*]*propenamide* **23**. The sulfone **23** was obtained as a 7:4 mixture of diastereoisomers as needles, m.p. 196–198 °C (from pentane–chloroform) after chromatography on silica gel using 3:1 light petroleum–ethyl acetate as eluent; $\delta_H(CDCl_3)$ 1.17–2.48 (10 H, complex 1′-H, 2′-H, 3′-H, 4′-H, 5′-H and 6′-H), 2.37 (3 H, s, Me-C_6H_4-, minor isomer), 2.45 (3 H, s, Me-C_6H_4-, major isomer), 2.70 (1 H, dd, *J* 9, 15, -SO_2CH_2-, major isomer), 3.05 (2 H, d, *J* 6, -SO_2CH_2-, minor isomer), 3.28 (1 H, dd, *J* 3, 15, -SO_2CH_2-, major isomer), 5.18 (1 H, s, 3-H, minor isomer), 5.33 (1 H, s, 3-H major isomer), 5.67 (1 H, s, 3-H, minor isomer), 5.69 (1 H, s, 3-H, major isomer), 7.13 (1 H, t, *J* 7, Ph), 7.22–7.40 (4 H, m, Ph and Ar), 7.56 (2 H, d, *J* 7, Ph, major isomer), 7.61 (2 H, d, *J* 7, Ph, minor isomer), 7.68 (2 H, d, *J* 8, Ar, minor isomer), 7.73 (2 H, d, *J* 8, Ar, major isomer), 7.80 (1 H, br s, NH, major isomer) and 8.10 (1 H, br s, NH, minor isomer); $\nu_{max}(CHCl_3)/cm^{-1}$ 3425, 3335 (NH), 1670 (C=O), 1599 (Ar), 1305 and 1145 (SO_2); *m/z* (NH_3 d.c.i.) 398 (100%, $M^+ + 1$) and 242 (76%, $M^+ - ArSO_2$).

N-*Phenyl*-5-(p-*tolylsulfonylmethyl*)*cyclohex*-1-*enecarboxamide* **25**. The sulfone **25** was obtained as an oil; $\delta_H(CDCl_3)$ 1.38–2.08 (2 H, m, 4-H), 2.10–2.70 (5 H, complex, 3-H, 5-H and 6-H), 2.47 (3 H, s, Me-C_6H_4), 3.08 (1 H, dd, *J* 6, 10, -SO_2CH_2-), 3.15 (1 H, dd, *J* 5, 10, -SO_2CH_2-), 6.68 (1 H, br s, 2-H), 7.10 (1 H, t, *J* 7, Ph), 7.25–7.42 (4 H, m, Ph and Ar), 7.53 (2 H, d, *J* 7, Ph), 7.62 (2 H, d, *J* 8, Ar) and 7.80 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3440, 3340 (NH), 1670 (C=O), 1598 (Ar), 1315 and 1150 (SO_2); *m/z* (NH_3 d.c.i.) 370 (100%, $M^+ + 1$) and 216 (71%).

N-*Phenyl*-2-[3′-(p-*tolylsulfonyl*)*cyclopentyl*]*propenamide* **21**. The sulfone **21** was obtained as a pair of diastereoisomers after column chromatography on silica gel using 3:1 light petroleum–ethyl acetate as eluent. The major diastereoisomer was isolated as a pale brown oil; $\delta_H(CDCl_3)$ 1.65–2.50 (6 H, complex, 2′-H, 4′-H and 5′-H), 2.47 (3 H, s, Me-C_6H_4-), 3.17 (1 H, m, 1′-H), 3.67 (1 H, m, 3′-H), 5.37 (1 H, s, 3-H), 5.67 (1 H, s, 3-H), 7.13 (1 H, t, *J* 7, Ph), 7.28–7.40 (4 H, m, Ph and Ar), 7.55 (2 H, d, *J* 7, Ph), 7.65 (1 H, br s, NH) and 7.78 (2 H, d, *J* 8, Ar); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430 (NH), 1675 (C=O), 1598 (Ar), 1305 and 1145 (SO_2); *m/z* (NH_3 d.c.i.) 387 (13%, $M^+ + 18$), 370 (100%, $M^+ + 1$) and 214 (22%, $M^+ - ArSO_2$). The minor diastereoisomer was obtained as needles, m.p. 132–134 °C (from pentane–chloroform); δ_H-($CDCl_3$) 1.67–2.38 (6 H, complex, 2′-H, 4′-H and 5′-H), 2.47 (3 H, s, Me-C_6H_4-), 3.12 (1 H, m, 1′-H), 3.63 (1 H, m, 3′-H), 5.50 (1 H, s, 3-H), 5.68 (1 H, s, 3-H), 7.14 (1 H, t, *J* 7, Ph), 7.30–7.42 (4 H, m, Ph and Ar), 7.57 (2 H, d, *J* 7, Ph), 7.60 (1 H, br s, NH) and 7.77 (2 H, d, *J* 8, Ar).

5,5-*Dimethyl*-N-*phenyl*-4-(p-*tolylsulfonyl*)*cyclohex*-1-*enecarboxamide* **27**. The sulfone **27** was isolated as needles, m.p. 69.5–71 °C (from pentane–chloroform) after chromatography on silica gel using 3:1 light petroleum–ethyl acetate as eluent; $\delta_H(CDCl_3)$ 1.28 (3 H, s, 5-Me), 1.40 (3 H, s, 5-Me), 2.18–2.75 (4 H, complex, 3-H and 6-H), 2.47 (3 H, s, Me-C_6H_4-), 3.10 (1 H, dd, *J* 4, 10, 4-H), 6.52 (1 H, br s, 2-H), 7.12 (1 H, t, *J* 7, Ph), 7.28–7.42 (5 H, m, Ph, Ar and NH), 7.52 (2 H, d, *J* 7, Ph) and 7.78 (2 H, d, *J* 8, Ar); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430 (NH), 1675 (C=O), 1599 (Ar), 1310 and 1145 (SO_2); *m/z* (NH_3 d.c.i.) 384 (88%, $M^+ + 1$), 230 (75%) and 228 (100%, $M^+ - ArSO_2$).

2-[2′,2′-*Dimethyl*-3′-(p-*tolylsulfonyl*)*cyclopentyl*]-N-*phenylpropenamide* **19**. The sulfone **19** was isolated as a 4:1 mixture of diastereoisomers as a pale yellow oil after chromatography on silica gel using 3:1 light petroleum–ethyl acetate as eluent; $\delta_H(CDCl_3)$ 1.15 (3 H, s, 2′-Me, major isomer), 1.18 (3 H, s, 2′-Me, minor isomer), 1.27 (3 H, s, 2′-Me, minor isomer), 1.50 (3 H, s, 2′-Me, major isomer), 1.72–2.33 (4 H, m, 4′-H and 5′-H), 2.47 (3 H, s, Me-C_6H_4-), 3.03–3.25 (2 H, m, 1′-H and 3′-H, both minor isomer), 3.19 (1 H, t, *J* 8, 1′-H or 3′-H, major isomer), 3.27 (1 H, dd, *J* 7, 10, 1′-H or 3′-H, major isomer), 5.32 (1 H, s, 3-H, major isomer), 5.40 (1 H, s, 3-H, minor isomer), 5.78 (1 H, s, 3-H, major isomer), 5.88 (1 H, s, 3-H, minor isomer), 7.15 (1 H, t, *J* 7, Ph), 7.30–7.40 (4 H, m, Ph and Ar), 7.48, 7.58 (2 H, d, *J* 7, Ph and 1 H, br s, NH) and 7.77 (2 H, d, *J* 8, Ar); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3330 (NH), 1675 (C=O), 1598 (Ar), 1305 and 1140 (SO_2); *m/z* (NH_3 d.c.i.) 415 (50%, $M^+ + 18$) 398 (100%, $M^+ + 1$) and 242 (47%, $M^+ - ArSO_2$).

2-[2′,2′-*Dimethyl*-3′-(p-*tolylsulfonyl*)*cyclohexyl*]-N-*phenylpropenamide* **29**. The *sulfone* **29** was obtained as a single diastereoisomer as needles, m.p. 170.5–172 °C (from pentane–chloroform) after chromatography on silica gel using 3:1 light petroleum–ethyl acetate as eluent (Found: C, 69.35; H, 7.05; N, 3.15. $C_{24}H_{29}NO_3S$ requires C, 70.05; H, 7.1; N, 3.4%); δ_H-($CDCl_3$) 1.28 (3 H, s, 2′-Me), 1.39 (3 H, s, 2′-Me), 1.47–1.98 (6 H, complex 4′-H, 5′-H and 6′-H), 2.47 (3 H, s, Me-C_6H_4-), 2.88 (1 H, dd, *J* 3, 13, 1′-H), 2.98 (1 H, dd, *J* 3, 12, 3′-H), 5.40 (1 H, s, 3-H), 5.90 (1 H, s, 3-H), 7.15 (1 H, t, *J* 7, Ph), 7.28–7.40 (4 H, m, Ph and Ar), 7.55 (2 H, d, *J* 7, Ph), 7.55 (2 H, d, *J* 8, Ar) and 7.73 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3455 (NH), 1675 (C=O), 1599 (Ar), 1305 and 1140 (SO_2); *m/z* (NH_3 d.c.i.) 412 (65%, $M^+ + 1$) and 258 (100%, $M^+ - ArSO_2$).

N-*Phenyl*-2-(p-*tolylthiomethyl*)*octa*-2,7-*dienamide* **36**. Sodium (63 mg) was added to methanol (10 cm^3) under nitrogen at 0 °C. When the sodium had dissolved, *p*-thiocresol (0.37 g) was added and the resulting solution was stirred for 10 min. 2-Methylene-*N*-phenyl-3-(*p*-tolylsulfonyl)oct-7-enamide **9** (0.11 g) was added and the solution was stirred for 2 h at 0 °C. Solvent was removed under reduced pressure, water was added and the solution extracted with ether (×2). The organic extracts were washed with dilute hydrochloric acid, water and brine, dried ($MgSO_4$) and evaporated under reduced pressure to give an oil.

Column chromatography using 5:1 light petroleum–ether as eluent gave the sulfide (95%) as an oil; $\delta_H(CDCl_3)$ 1.28–1.43 (2 H, m, 5-H), 1.88–2.04 (4 H, m, 4-H and 6-H), 2.33 (3 H, s, Me-C_6H_4-), 3.83 (2 H, s, -SCH_2-), 4.93–5.05 (2 H, m, 8-H), 5.65–5.83 (1 H, m, 7-H), 6.53 (1 H, t, *J* 8, 3-H), 7.08–7.17 (3 H, m, Ph and Ar), 7.28–7.40 (4 H, m, Ph and Ar), 7.55 (2 H, d, *J* 8, Ph) and 8.28 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3425, 3305 (NH), 2912 (CH), 1670 (C=O) and 1598 (Ar); *m/z* (NH_3 d.c.i.) 352 (100%, $M^+ + 1$).

N-*Phenyl*-2-(p-*tolylsulfinylmethyl*)*octa*-2,7-*dienamide* **37**. Hydrogen peroxide (100 vol, 0.1 cm^3, 4.5 equiv.) was added to a stirred solution of sulfide **36** (61.5 mg) in methanol (7 cm^3) at 20 °C. After 4 days, brine was added, the mixture was extracted with chloroform (×3), dried ($MgSO_4$) and evaporated under reduced pressure to give an oil. Column chromatography using 3:1 light petroleum–ether then 3:1 light petroleum–ethyl acetate as eluents gave the sulfoxide **37** (67%) as an oil (10:1 mixture of *E*:*Z* isomers, NMR spectroscopic data quoted is that for the *E*-isomer only); $\delta_H(CDCl_3)$ 1.37–1.55 (2 H, m, 5-H), 1.70–2.13 (4 H, and 6-H), 2.40 (3 H, s, Me-C_6H_4-), 3.79 (1 H, d, *J* 13, -$SOCH_AH_B$-), 3.95 (1 H, d, *J* 13, $SOCH_AH_B$-), 4.90–5.07 (2 H, m, 8-H), 5.63–5.81 (1 H, m, 7-H), 6.85 (1 H, t, *J* 7, 3-H), 7.10 (1 H, t, *J* 7, Ph), 7.25–7.40 (4 H, m, Ph and Ar), 7.53 (2 H, d, *J* 8, Ph), 7.62 (2 H, d, *J* 7, Ar) and 9.75 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3009 (CH), 1670 (C=O), 1599 (Ar) and 1030; *m/z* (NH_3 d.c.i.) 368 (100%, $M^+ + 1$), 246 (61%), 230 (63%) and 228 (82%, $M^+ - ArSO$).

Attempted cyclisation of sulfide **36** *and sulfoxide* **37**. Benzoyl peroxide (*ca.* 2 mg) was added to a solution of either sulfide **36** or sulfoxide **37** (*ca.* 4 mg) in cyclohexane or *tert*-butanol respectively in a 5 mm NMR tube. The resulting solution was heated to 85 °C (oil bath temperature) and the reaction was monitored by ^1H NMR spectroscopy. After 30 h there was no spectroscopic evidence that any cyclised product had been formed.

N-*Phenyl*-2-(p-*tolylsulfonylmethyl*)*but*-2-*enamide* **35**. The sulfone **35** was prepared from sulfone **34** (0.05 g) and sodium toluene-*p*-sulfinate (0.25 g) in aq. AcOH (Method B). The crude product was purified by chromatography on silica gel using 3:1 light petroleum–ethyl acetate as eluent to give the sulfone **35** (96%) as an oil, a 9:2 mixture of diastereoisomers; $\delta_H(CDCl_3)$ 1.68 (3 H, d, *J* 7, 4-H, major isomer), 1.97 (3 H, d, *J* 7, 4-H, minor isomer), 2.38 (3 H, s, Me-C_6H_4-, major isomer), 2.42 (3 H, s, Me-C_6H_4-, minor isomer), 4.04 (2 H, s, -SO_2CH_2-, minor isomer), 4.28 (2 H, s, -SO_2CH_2-, major isomer), 5.87 (1 H, q, *J* 7, 3-H minor isomer), 6.88 (1 H, q, *J* 7, 3-H, major isomer), 7.05–7.17 (1 H, m, Ph), 7.25–7.34 (4 H, m, Ph and Ar), 7.48 (2 H, d, *J* 7, Ph, major isomer), 7.57 (2 H, d, *J* 7, Ph, minor isomer), 7.78 (2 H, d, *J* 8, Ar), 8.57 (1 H, br s, NH, major isomer) and 8.80 (1 H, br s, NH, minor isomer); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3320 (NH), 1720 (C=O), 1598 (Ar), 1315 and 1140 (SO_2); *m/z* (NH_3 d.c.i.) 347 (51%, $M^+ + 18$), 330 (100%, $M^+ + 1$) and 176 (53%).

N-*Phenyl*-2-(p-*tolylsulfonylmethyl*)*propanamide* **33**. The sulfone **33** was prepared from 2-methyl-*N*-phenylpropenamide **32** (0.04 g) and sodium toluene-*p*-sulfinate (0.42 g) in aq. AcOH (Method B) as an oil (49%) after chromatography on silica gel using 4:1 light petroleum–ethyl acetate as eluent; $\delta_H(CDCl_3)$ 1.40 (3 H, d, *J* 6.5, 3-H), 2.38 (3 H, s, Me-C_6H_4-), 3.06–3.23 (2 H, m, -SO_2CH_2- and 2-H), 3.83 (1 H, dd, *J* 9, 14, SO_2CH_2-), 7.10 (1 H, t, *J* 7, Ph), 7.25–7.33 (4 H, m, Ph and Ar), 7.43 (2 H, d, *J* 7, Ph), 7.80 (2 H, J 8, Ar) and 7.85 (1 H, br s, NH); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430, 3340 (NH), 1680 (C=O), 1600 (Ar), 1305 and 1145 (SO_2); *m/z* (NH_3 d.c.i.) 318 (100%, $M^+ + 1$), 162 (26%, $M^+ - ArSO_2$), 139 (22%, $ArSO^+$) and 93 (18%, $PhNH_2^+$).

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