Fragmentation Patterns in the Gas-phase Pyrolysis of Some Bi- and Tri-cyclic Sulfolanes Related to the 8-Thiabicyclo[4.3.0]non-3-ene 8,8-Dioxide Ring System

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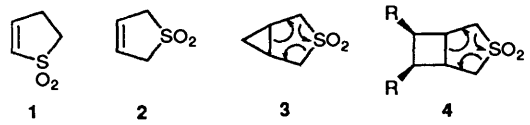
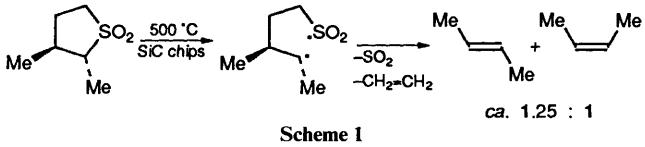
Depending upon the degree of ring strain, the thermal breakdown of *cis*-8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide **5** and related ring systems in the gas phase follows widely differing pathways. Decomposition of **5** occurs only under forcing conditions, resulting in complete fragmentation of the sulfolane ring to give benzene and toluene, while pyrolysis of the 2,5-bridged analogues **6–8** proceeds by a retro-Diels–Alder reaction at much lower temperatures to give 1,3-dienes and the decomposition products of 3-sulfolene, buta-1,3-diene and SO_2. Epoxidation of the double bond in these compounds results in a marked change in their thermal fragmentation behaviour; only SO_2 is lost to produce novel divinyl epoxides. The corresponding *N*-ethoxycarbonylaziridines, formed by photolysis of the unsaturated sulfones in ethyl azidoformate, undergo extensive decomposition on pyrolysis and do not yield any useful products. The saturated sulfone **28** gives the expected octa-1,7-diene upon flash vacuum pyrolysis (FVP), but only under relatively severe conditions. Three isomeric diene sulfones **30–32** have also been examined and show a varied pattern of reactivity under FVP conditions.

A large number of reactions involving thermal extrusion of SO_2 from cyclic sulfones are now known, many of which find application not only in the synthesis of natural products, but also for many highly reactive compounds that are not accessible by other methods.[1] In a previous paper[2] we exploited the gas-phase elimination of SO_2 (and ethylene) from Diels–Alder adducts of 2-sulfolene **1** as a means of achieving acetylene



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

equivalency. This paper contains an account of a parallel investigation into the pyrolytic removal of SO_2 from the corresponding derivatives of 3-sulfolene **2** for which concomitant loss of ethylene is not possible. Where simple monocyclic sulfolanes are concerned, pyrolysis normally leads to fragmentation *via* an initial diradical as depicted in Scheme 1 to give

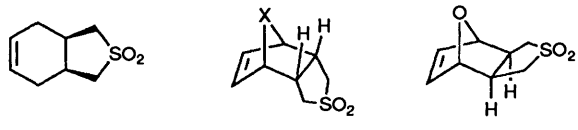


Scheme 1

alkenes and SO_2.[3] Based on the limited information available for bicyclic systems less forcing conditions are required for the removal of SO_2. The bicyclic compound **3** is reported[4] to decompose smoothly to give penta-1,4-diene and SO_2 in a concerted $\sigma^2s + \sigma^2s + \sigma^2s$ process, while we have shown that when a four-membered ring is fused to the sulfolane system as in **4**, thermal loss of SO_2 results in a facile ring cleavage, probably by a similar mechanism, to produce *cis*-1,2-divinyl compounds,[5] which for acyclic analogues spontaneously rearrange with a high degree of stereoselectivity to *E,Z*-1,5-dienes.[6] Similar studies in which the sulfolane ring forms part of a larger, fused bridged ring system, as described here, have so far not been reported.

Results and Discussion

Whereas the Δ^1-isomer **1** showed some ability to enter into (4 + 2)π reactions as a moderately reactive dienophile, all attempts to prepare the adducts **5–8** by reaction of the



5 **6** X = CH_2, **7** X = CH_2CH_2 **8**

corresponding 1,3-diene with **2** ended in failure. Prolonged heating of the reagents under forcing conditions, either in the presence or absence of $SnCl_4$ as catalyst, gave no evidence of product formation; either destruction of **2** occurred, or else the 1,3-diene underwent self-condensation. Cycloaddition to 2,5-dihydrothiophene and subsequent oxidation did offer access to the desired compounds, but the yields in the initial step were disappointingly low, *e.g.* only 25% in the case of cyclopentadiene.[7] Much better results were obtained by making recourse to the more powerful dienophilic properties of maleic anhydride and the sequence of reactions shown in Scheme 2. The overall yields ranged from 38% for **5** to 16% for **8**. The sulfones are sweet-smelling, highly crystalline solids with all the expected analytical and spectral properties, including IR absorptions at 1300 and 1150–1100 cm^{-1} for the sulfone groupings. Based on the reasonable assumption that the transformations in Scheme 2 provide no opportunity for isomerisation, the compounds were assigned the same stereochemistry as the products of the addition of maleic anhydride

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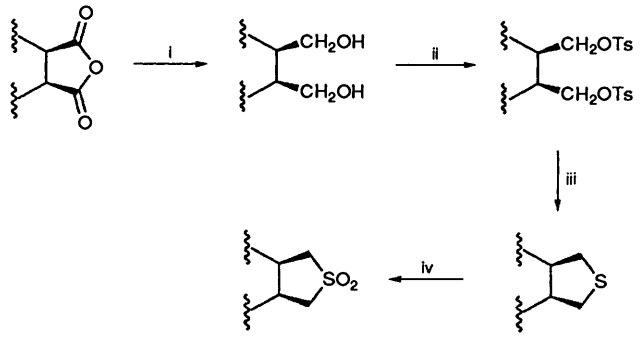
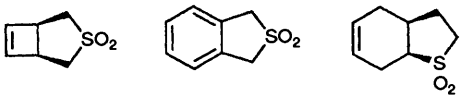


Scheme 2 *Reagents:* i, $LiAlH_4$, THF; ii, TsCl, pyridine; iii, Na_2S, $EtOH–H_2O$ (1:1); iv, MCPBA, Et_2O (Ts = *p*-$MeC_6H_4SO_2$)

to the 1,3-dienes, *viz.* **5** is *cis*,[8] **6** and **7** are *endo*,[8] while the furan–maleic anhydride adduct which has been shown to be *exo*,[9] gives rise to the *exo*-configuration for **8**.

When heated above its melting point, the bicyclic sulfone **5** showed no tendency to decompose, and even under flash vacuum pyrolysis (FVP) conditions, thermal elimination of SO_2 proved to be very difficult. At 750 °C and 0.001 mmHg, the compound passed through the furnace unchanged, and by raising the temperature to 850 °C to bring about complete fragmentation of the sulfolane ring, aromatisation occurred to give benzene (33%) and toluene (29%), together with five minor unidentifiable products (total 8%). The severity of the conditions compares unfavourably with the relative ease with which SO_2 is extruded from the four-membered ring homologue **9**[10] and the aromatic-fused system **10**.[11] At 400 °C and 10^{-3}



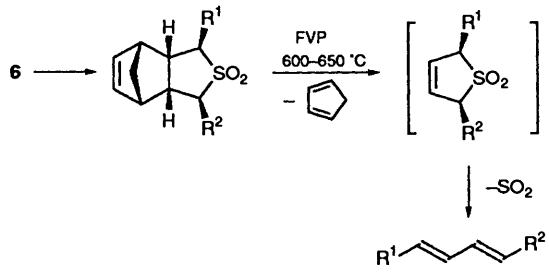
9 **10** **11**

mmHg, **9** decomposes cleanly to afford a *ca.* 1:1 mixture of *cis*-hexa-1,3,5-triene and its electrocyclised product, cyclohexa-1,3-diene, in virtually quantitative yield, whilst SO_2 is similarly lost from **10** at 500 °C to give benzocyclobutene in 60% yield. An explanation for the high thermal stability of **5** may lie in the flexibility associated with the six-membered ring of the *cis*-bicyclo[4.3.0]non-3-ene system,[12] allowing it to adopt a conformation whereby the sulfone ring is placed under much less strain than that in either **9** or **10**. Another contributing factor is that the elimination of SO_2 from **5** probably proceeds by a radical mechanism, whereas for **9** and **10** loss of SO_2 is believed to be cheleotropic in nature and hence a lower energy process. Similar considerations point to a concerted reaction for the thermal fragmentation of the isomeric sulfone **11** which gave cyclohexa-1,4-diene at the relatively low pyrolysis temperature of 675 °C by simultaneous loss of SO_2 and ethylene.[2]

Somewhat less forcing conditions were required to decompose the tricyclic sulfones **6–8**. Fragmentation occurred smoothly at 675 °C for **6** and **8**, and at the higher temperature of 750 °C for the much less strained two carbon-bridged sulfone **7**, but in each case, the gain in stabilisation achieved by eliminating a 1,3-diene led to an almost quantitative [4π + 2π] cycloreversion reaction rather than the desired extrusion of SO_2. From separate pyrolysis experiments, the co-produced 3-sulfolene was shown to decompose quantitatively under the reaction conditions to give SO_2 and buta-1,3-diene which was isolated in yields up to 50% depending on how quickly the pyrolysate could be removed from the cold trap.

In the pyrolysis of **6** and **7**, considerable loss of products was encountered due to the formation of a colourless, insoluble, polymer-like material in the cold trap. A report has appeared in the literature[13] that cyclohexa-1,3-diene rapidly forms a 1:1 co-polymer with SO_2 at temperatures as low as −50 °C. Elemental analysis of the solid from the pyrolysis of **7** indicated that it was a 1:1 co-polymer to a good approximation. Similarly, the solid from the pyrolysis of **6** gave an analysis in good agreement with that expected for $C_5H_6O_2S$, a 1:1 copolymer of cyclopentadiene and SO_2.

In the present context, the foregoing cycloreversion reactions are of no preparative value, but while this work was in progress, Bloch and Abecassis[14] reported a high-yielding and stereospecific synthesis of *E,E*-1,4-disubstituted 1,3-dienes (Scheme 3)

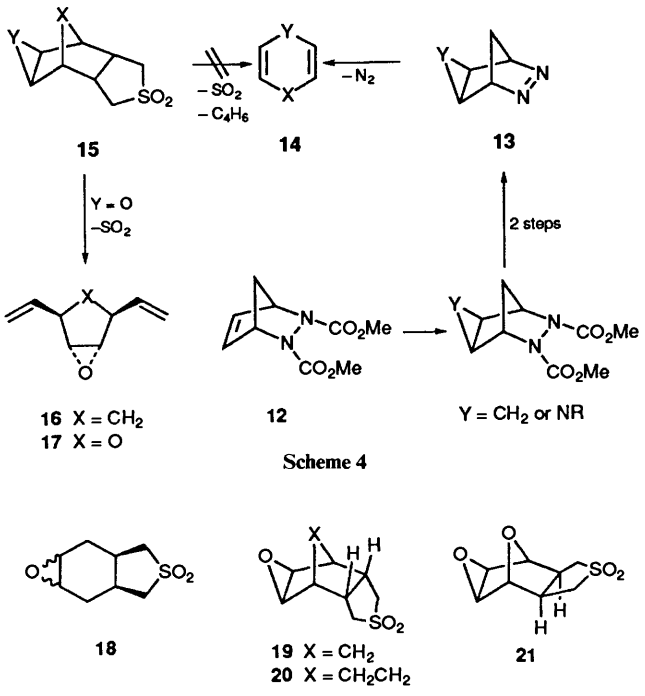


Scheme 3

based on the alkylation of **6** alpha to the sulfone function prior to thermal fragmentation under FVP conditions. This approach was devised to circumvent the problems associated with the extreme lability of 3-sulfolene itself under basic conditions, but recently Yamada *et al.*[15] and Chou *et al.*[16] have shown that such decomposition can be suppressed by judicious use of lithium diisopropylamide and sodium hydride, respectively at −78 °C in the presence of the alkylating agent.

Many other examples like the aforementioned diene synthesis are known in which the sequence of Diels–Alder reaction, modification of the dienophile part of the adduct, and subsequent cycloreversion, has allowed high yield access to key compounds.[17] In each case, the Diels–Alder adduct is simply used to protect the dienophile double bond. Much less common is the corresponding sequence of reactions involving the modification of the diene part of the adduct, probably because the most obvious change—functionalisation of the double bond—means that the retro-reaction no longer gives rise to a diene and much of the driving force for its removal is lost. The only examples in which this strategy appears to have been successful involve the elimination of nitrogen *via* the cyclopentadiene adduct **12** of dimethyl azodicarboxylate. In this instance elaboration of the double bond to a cyclopropane moiety[18] or to an aziridine[19] followed by conversion into the azo compound **13** and thermolysis as shown in Scheme 4, produced cyclohexa-1,4-diene and a dihydropyridine, respectively. A feature of this particular procedure is that two steps are required to convert the initial dienophile into an easily extrudable fragment, in this case nitrogen. We anticipated that sulfones **6–8** might provide a convenient alternative to the use of **12** whereby elaboration of the double bond to give compounds **15** would afford products of the type **14** directly by thermal loss of SO_2 and butadiene.

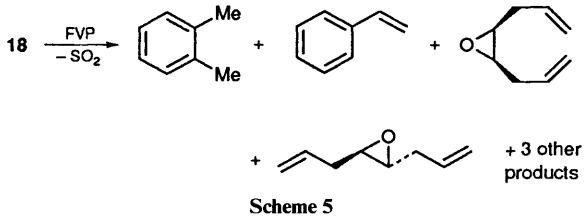
With this strategy in mind, the epoxides **18–21** were prepared by oxidation with *m*-chloroperoxybenzoic acid in boiling ethyl acetate for **5** and **7** and with peracetic acid for **6** and **8**. The choice of oxidising agent was found to be important as, for example, treatment of **5** and **7** with performic acid, resulted in cleavage of the epoxide to give a diol monoester, while **6** and **7** failed to react with *m*-chloroperoxybenzoic acid at room temperature. The ^1H NMR spectra of the epoxides all showed a characteristic sharp singlet at δ 3.4–3.2 due to the epoxide



Scheme 4

protons, while the mass spectra of **6**, **7** and **8** all showed prominent peaks at $M^+ - 118$ corresponding to the loss of SO_2 and butadiene and the formation of heterocyclic systems such as **14** (Y = O).

When these compounds were subjected to FVP, an entirely different mode of fragmentation was observed. Only SO_2 was extruded, to give in the case of **18** at 725 °C, a pungent colourless liquid, which by GLC analysis, contained seven components. Two of these were positively identified as styrene and *o*-xylene, while GC–MS suggested that the two least volatile components, with molecular ion peaks at m/z = 124, might be the *cis*- and *trans*-isomers of diallyloxirane (4,5-epoxyocta-1,7-diene). Further evidence in support of these structures came from a large-scale pyrolysis which gave a sample with ^1H and ^{13}C NMR signals corresponding to the pattern expected for diallyloxirane. The pyrolytic breakdown for **18** is summarised in Scheme 5. The formation of styrene deserves some comment



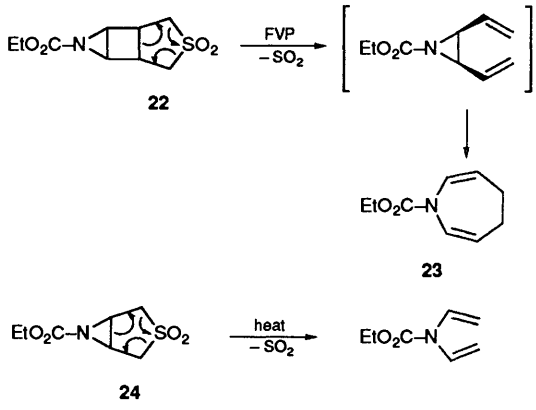
Scheme 5

since it implies the occcurrence of a ring closure step after the extrusion of SO_2 to form a cyclobutane intermediate, a process analogous to the fragmentation of **10** (*vide supra*).

The methylene- and oxygen-bridged epoxides **19** and **21** lost SO_2 with relative ease at 700 °C to produce the novel *cis*-divinyl epoxides **16** and **17** as depicted in Scheme 4, in yields of 39 and 61% respectively, and in high purity as determined by their ^{13}C NMR spectra. Each compound was present as a single isomer and from the stereochemistry of the starting sulfones, the vinyl groups are presumed to be *trans* to the epoxide ring in both cases.

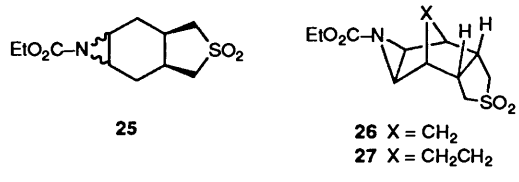
As with **18**, significant side-reactions occurred during the thermal decomposition of epoxide **20** at 700 °C. Again, no pure compounds could be isolated, although the ^{13}C NMR spectrum of the distilled pyrolysate showed the presence of four distinct vinyl signals as well as a carbonyl group. Compared with **19** and **21**, these epoxides are much less strained and this may well account for the increase in side-reactions by making the extrusion of SO_2 a more difficult process, other than by radical cleavage.

As described earlier, aziridines derived from **12** have been used to prepare dihydropyridines. In an earlier communication[12] we reported that pyrolysis of the aziridine **22** (derived from **9**) offered access to the 4,5-dihydroazepine **23**, whilst



Meyers and Takaya[20] have similarly used the thermal elimination of SO_2 from the aziridine **24** (derived from 3-sulfolene **2**) in a synthesis of divinyl carbamates.

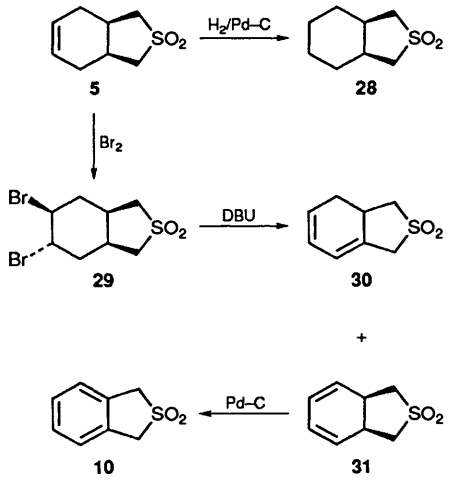
Photolysis of the unsaturated sulfones **5**–**7** with ethyl azidoformate in the absence of solvent afforded the corresponding *N*-ethoxycarbonylaziridines **25**–**27** in moderate yields. Under similar conditions, the oxygen-bridged sulfone **8** gave none of the desired aziridine. In the case of **25**, the compound was formed as a 1:1 mixture of *syn*- and *anti*-isomers as indicated by the presence of separate ^1H NMR signals for the ethyl-CH_2 and epoxide protons in each isomer. In **26** and **27** no such effect was observed and these are assumed to exist as the *exo*-aziridine isomers entirely.



Pyrolysis of **25**–**27** surprisingly yielded no useful products. In each case extensive decomposition took place to give products derived from the complete breakdown of both the aziridine function and the carbon skeleton. Thus, pyrolysis of **25** at 725 °C led to decomposition with the formation of tar in the inlet tube corresponding to one-third of the starting material. The volatile products consisted of a complex mixture in which only ethanol could be positively identified. Thermal breakdown of **26** at 675 °C and **27** at 725 °C gave similar results. In each case the pyrolysate contained at least thirteen compounds, including ethanol and ethyl carbamate, together with *o*-xylene and indene in the former case, and benzene and styrene in the latter. Thus, it appears that, while aziridines such as **22** and **24** can be pyrolysed to give useful products, the aziridine function is too unstable to survive the more forcing conditions required to extrude SO_2 from the less strained compounds **25**–**27**, which presumably fragment by more indiscriminate radical pathways.

In view of the resistance of **5** towards thermal extrusion of SO_2, which as mentioned earlier, contrasts with the behaviour

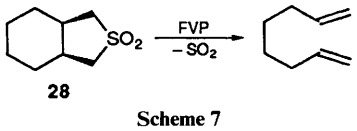
of closely related compounds such as **9**–**11**, it was of interest to examine the behaviour of analogues such as the saturated sulfone **28** and the diene sulfones **30**–**32** under FVP conditions. The compounds were readily prepared, as shown in Scheme 6,



Scheme 6

by catalytic hydrogenation of **5** which gave **28**, and by bromination of **5** to form **29** followed by dehydrobromination using DBU, which gave both **30** and **31**. An attempt to prepare **31** in pure form by the route of Scheme 2 starting from *cis*-1,2-dihydrophthalic anhydride[21] was not successful due to problems in the reaction of the bis(toluene-*p*-sulfonate) with Na_2S. Even using Na_2S in anhydrous HMPA,[22] gave a consistently poor yield of product contaminated by the fully aromatic sulfide. The route of Scheme 2 was however successful in producing the *trans* diene sulfone **32** beginning from the diol obtained by $LiAlH_4$ reduction of *trans*-dihydrophthalic acid.[21] As expected the *cis* diene sulfone **31** was readily oxidised in the presence of Pd/C to give **10**.

The saturated sulfone **28** was relatively resistant to SO_2 extrusion and was recovered completely unchanged on FVP at 650 °C while even at 850 °C there was 13% recovery of unchanged **28**. The major product in the latter case, obtained in 41% yield, was the expected octa-1,7-diene (Scheme 7) and this

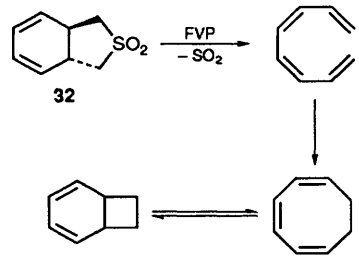


Scheme 7

was accompanied by small quantities of benzene and buta-1,3-diene. At 925 °C the starting material was completely consumed and the main product was again octa-1,7-diene (20%), although the proportions of benzene and butadiene had increased and further unidentified products and polymers became more significant. The thermal stability of **28**, which closely matches that of **5** described earlier, can again be attributed to the relatively low degree of ring-strain present.

The three isomeric diene sulfones **30**–**32** showed a surprisingly diverse and complex pattern of behaviour on FVP. The 1,3-compound **30** was half unchanged even at 850 °C and the major products were styrene and toluene, accompanied by smaller quantities of ethylbenzene, *o*-xylene and benzene. On increasing the temperature to 900 °C, only 17% of the sulfone was unchanged and the other products were the same, while at 950 °C complete reaction occurred to give styrene (37%), toluene (35%), benzene (11%), ethylbenzene (5%) and smaller quantities of *o*-xylene and unidentified materials. The *cis*-2,4-compound **31** was recovered unchanged from FVP at 625 °C and even at 850 °C it only reacted to an extent of 85% to give benzene as the main product (50%) accompanied by styrene (11%), ethylbenzene (8%), *o*-xylene (5%) and lesser quantities of toluene and unidentified components. In complete contrast to these examples, the *trans*-2,4-compound **32** underwent complete extrusion of SO_2 at 650 °C to give as the main product (65%) a compound assigned on the basis of ^1H NMR and GC–MS data to be cycloocta-1,3,5-triene **33** accompanied by its bicyclic isomer **34**. The other products in this case were *o*-xylene (14%), benzocyclobutene (4%) and styrene (2%).

The last example **32** is clearly the only one for which there is sufficient ring strain present to allow SO_2 extrusion at a relatively low temperature and therefore to give a relatively clean product. As shown in Scheme 8, extrusion of SO_2 is



Scheme 8

believed to initially generate the *Z*,*Z*-octatetraene which is known[23] to undergo rapid cyclisation to the cycloocta-1,3,5-triene **33**, a species itself in equilibrium[24,25] with the bicyclic isomer **34**. Secondary reactions of **34** could well account for the formation of benzocyclobutene and styrene as minor products while the *o*-xylene most likely results from hydrogen atom transfer in the diradical formed by extrusion of SO_2 from **32**. The same intermediates could be involved to some extent in the reactions of **30** and **31** since it is known, for example, that further heating of the **33**–**34** mixture results in extrusion of ethene to give benzene.[26] Also pyrolysis of *E*,*E*-octatetraene leads *via* isomerisation to the *E*,*Z* form and cyclisation to give 5-vinylcyclohexa-1,3-diene, both to 1-vinylcyclohexa-1,3-diene and its tricyclic intramolecular Diels–Alder product and to styrene.[25] The formation of 1-vinylcyclohexene from **33**–**34** has also been demonstrated.[27] Intramolecular hydrogen atom transfer in either of the isomeric vinylcyclohexadienes could be the source of the ethylbenzene obtained from both **30** and **31**. This leaves *o*-xylene and toluene to be explained, and it is suggested that the former results from hydrogen atom transfers within the diradical formed by loss of SO_2 from both **30** and **31**, while the latter may be formed by initial extrusion of sulfene, $CH_2{=}SO_2$, rather than SO_2 from the sulfones. Further detailed studies employing isotopically labelled substrates would be required to unambiguously determine the processes involved in these pyrolyses.

Experimental

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. Ultraviolet spectra were recorded using matched 1 cm quartz cells on a Unicam SP800A spectrophotometer. Infrared spectra were recorded for Nujol mulls on a Perkin-Elmer 157G spectrophotometer. NMR spectra were recorded for ^1H at 100 MHz on a Varian HA100 instrument or at 360 MHz on a Bruker WH360 instrument and for ^{13}C at 20 MHz on a Varian CFT 20 or at 90 MHz on a Bruker WH360 instrument. In ^{13}C NMR spectra 4ry represents quaternary carbon. Spectra were obtained for solutions in $CDCl_3$ unless otherwise indicated with Me_4Si as internal

standard. Coupling constants J are given in Hz. Mass spectra were obtained on a AEI MS902 instrument using electron impact at 70 eV. GC–MS was performed with a Pye 104 chromatograph coupled to a VG Micromass 12 spectrometer. Ether refers to diethyl ether.

Preparation of Unsaturated Sulfones **5–8**.—(a) cis-8-*Thiabicyclo*[4.3.0]*non*-3-*ene* 8,8-*dioxide* **5**. (i) *cis*-8-Thiabicyclo-[4.3.0]non-3-ene. This compound was prepared by the literature procedure[12] as a colourless oil, b.p. 83–84 °C/0.6 mmHg (lit.,[12] 121–125 °C/10 mmHg) (Found: C, 68.7; H, 8.6. Calc. for $C_8H_{12}S$: 68.5; H, 8.5%).

(ii) cis-8-*Thiabicyclo*[4.3.0]*non*-3-*ene* 8,8-*dioxide* **5**. A solution of the sulfide (4.48 g, 32 mmol) in dry ether (50 cm^3) was stirred at 0 °C while a solution of *m*-chloroperoxybenzoic acid (MCPBA) (85%, 13.0 g, 64 mmol) in dry ether (200 cm^3) was added dropwise. The solution was stirred at room temperature for 60 h and then washed well with aqueous sodium carbonate, dried, and evaporated. Recrystallisation of the residue from ether gave the *title compound* **5** (4.11 g, 75%) as colourless needles, m.p. 73–74 °C (Found: C, 55.95; H, 7.05. $C_8H_{12}O_2S$ requires C, 55.8; H, 7.0%); ν_{max}/cm^{-1} 1290, 1110, 953, 890, 831, 780, 751 and 728; δ_H 5.66 (2 H, t, J 2), 3.28–2.88 (4 H, m), 2.70 (2 H, m) and 2.26 (4 H, m); m/z 172 (M^+, 50%), 155 (13), 107 (35), 106 (62), 105 (23), 92 (23), 91 (90), 79 (100), 78 (32) and 77 (32).

(b) endo-4-*Thiatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* 4,4-*dioxide* **6**. (i) *endo*-4-Thiatricyclo[5.2.1.$0^{2,6}$]dec-8-ene. This compound was prepared by the literature procedure[28] as a colourless oil, b.p. 228–229 °C/760 mmHg, n_D^{20} 1.5490 (lit.,[28] 57 °C/0.45 mmHg, n_D^{26} 1.5546) (Found: C, 70.8; H, 8.1. Calc. for $C_9H_{12}S$: C, 71.0; H, 7.9%).

(ii) endo-4-*Thiatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* 4,4-*dioxide* **6**. A solution of the sulfide (5.50 g, 36.2 mmol) in dry ether (125 cm^3) was stirred at 0 °C while a solution of *m*-chloroperoxybenzoic acid (85%; 14.9 g, 73.5 mmol) in dry ether (400 cm^3) was added dropwise. The solution was stirred at room temperature for 75 h and then washed well with aqueous sodium carbonate, dried and evaporated. Recrystallisation of the residue from ethanol gave the *title compound* **6** (3.16 g, 48%) as colourless flakes, m.p. 124–126 °C (lit.,[7] 114–116 °C, not characterised) (Found: C, 58.95; H, 6.65. $C_9H_{12}O_2S$ requires C, 58.7; H, 6.6%); ν_{max}/cm^{-1} 1312, 1257, 1228, 1150, 1108, 942, 910, 854, 849, 791 and 762; δ_H 6.23 (2 H, t, J 2), 3.04 (4 H, s), 3.3–2.8 (2 H, m), 2.4–2.2 (2 H, m) and 1.76 and 1.47 (2 H, AB pattern, J 9); m/z 184 (M^+, 1.5%), 156 (18), 139 (1.5), 105 (7), 103 (1.5), 91 (8), 79 (6), 77 (7) and 66 (100, cyclopentadiene).

(c) endo-4-*Thiatricyclo*[5.2.2.$0^{2,6}$]*undec*-8-*ene* 4,4-*dioxide* **7**. (i) A solution of *endo*-5,6-bis(*p*-tolylsulfonyloxymethyl)bicyclo-[2.2.2]oct-2-ene[29] (10.27 g, 21.6 mmol) and sodium sulfide nonahydrate (15.5 g, 64.6 mmol) in ethanol (50 cm^3) and water (50 cm^3) was boiled under reflux for 12 h. After removal of the ethanol under reduced pressure, the residue was extracted with dichloromethane. Drying and evaporation followed by Kugelrohr distillation gave endo-4-*thiatricyclo*[5.2.2.$0^{2,6}$]*undec*-8-*ene* (2.46 g, 69%) as a colourless oil, b.p. 246–248 °C/760 mmHg, n_D^{25} 1.5350 (Found: C, 72.25; H, 8.5. $C_{10}H_{14}S$ requires C, 72.2; H, 8.5%); ν_{max}/cm^{-1} 3040, 2930, 2860, 1460, 1435, 1250, 1200, 915, 850, 817, 732 and 710; δ_H 6.13 (2 H, t, J 4), 2.50 (6 H, s), 1.48 and 1.28 (4 H, A_2B_2 pattern, J 10) and 1.25 (2 H, s); m/z 166 (M^+, 90%), 119 (15), 92 (18), 91 (48), 87 (38), 85 (21), 84 (81), 83 (15), 80 (100) and 79 (75).

(ii) endo-4-*Thiatricyclo*[5.2.2.$0^{2,6}$]*undec*-8-*ene* 4,4-*dioxide* **7**. A solution of the sulfide (2.20 g, 13.25 mmol) in dry ether (50 cm^3) was stirred at 0 °C while a solution of *m*-chloroperoxybenzoic acid (85%, 5.46 g, 16.9 mmol) in dry ether (150 cm^3) was added dropwise. After being stirred at room temperature for 60 h, the solution was washed well with aqueous sodium carbonate, dried and evaporated. Recrystallisation of the residue from ether gave the *title compound* **7** (1.98 g, 76%) as colourless crystals, m.p. 112–113 °C (Found: C, 60.9; H, 7.3. $C_{10}H_{14}O_2S$ requires C, 60.6; H, 7.1%); ν_{max}/cm^{-1} 1377, 1317, 1293, 1247, 1197, 1148, 1096, 890, 739, 730 and 714; δ_H 6.30 (2 H, t, J 4), 3.08–2.97 (2 H, m), 2.61 (6 H, m) and 1.61 and 1.38 (4 H, A_2B_2 pattern, J 11); m/z 198 (M^+, 14%), 105 (6), 104 (3), 91 (16), 80 (100) and 79 (18).

(d) exo-10-*Oxa*-4-*thiatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* 4,4-*dioxide* **8**. (i) exo-5,6-*Bis*(p-*tolylsulfonyloxymethyl*)-7-*oxabicyclo*-[2.2.1]*hept*-2-*ene*. A solution of *exo*-5,6-bis(hydroxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene[30] (8.20 g, 52.6 mmol) in pyridine (50 cm^3) was added slowly to a stirred suspension of toluene-*p*-sulfonyl chloride (32.6 g, 169 mmol) in pyridine (50 cm^3) at 0 °C. After being stirred at 0 °C for 3 h the mixture was poured into water (250 cm^3). The resulting precipitate was filtered off, washed with dilute sulfuric acid and then water, and dried. Recrystallisation from hexane–chloroform gave the *title compound* (20.3 g, 83%) as colourless needles, m.p. 145–146 °C (decomp.) (Found: C, 57.0; H, 5.2. $C_{22}H_{24}O_7S_2$ requires C, 56.9; H, 5.2%); ν_{max}/cm^{-1} 1597, 1355, 1170, 1098, 950, 885, 862, 820, 689 and 668; δ_H 7.75 and 7.34 (8 H, A_2B_2 patterns, J 8), 6.30 (2 H, s), 4.68 (2 H, s), 4.2–3.8 (4 H, m), 2.45 (6 H, s) and 2.15–1.95 (2 H, m); m/z no peaks above 172 (27%, TsOH) 155 (4), 120 (4), 108 (22), 107 (33), 92 (10) and 91 (100).

(ii) exo-10-*Oxa*-4-*thiatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene*. A solution of the bis-tosyl ester (21.0 g, 45.3 mmol) and sodium sulfide nonahydrate (32.6 g, 136 mmol) in ethanol (125 cm^3) and water (125 cm^3) was boiled under reflux for 60 h. The ethanol was removed under reduced pressure and the residue extracted with dichloromethane (3 × 100 cm^3). Drying and evaporation gave the crude product (4.33 g, 62%) as a low-melting solid. Vacuum sublimation of a sample at 50–70 °C/0.05 mmHg gave the *title compound* (38% recovery) as colourless needles, m.p. 45–47 °C (Found: C, 62.05; H, 6.6. $C_8H_{10}OS$ requires C, 62.3; H, 6.5%); ν_{max}(melt)/cm^{-1} 2980, 2960, 2910, 2437, 1304, 1267, 1255, 1235, 1120, 1090, 1043, 991, 939, 897, 803, 789 and 688; δ_H 6.34 (2 H, s), 4.58 (2 H, s) and 2.95–2.6 (6 H, m); m/z 154 (M^+, 26%), 88 (5), 87 (8), 86 (100, dihydrothiophene), 85 (57), 79 (5), 77 (6), 69 (8) and 68 (21, furan).

(iii) exo-10-*Oxa*-4-*thiatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*ene* 4,4-*dioxide* **8**. A solution of the crude sulfide (3.33 g, 21.6 mmol) in dry dichloromethane (75 cm^3) was stirred at 0 °C while a solution of *m*-chloroperoxybenzoic acid (85%; 8.90 g, 43.9 mmol) in dry dichloromethane (50 cm^3) was added dropwise. After being stirred at room temperature for 18 h the solution was washed well with aqueous sodium carbonate, dried and evaporated. Recrystallisation of the residue from ethanol gave the *title compound* **8** (1.95 g, 49%) as colourless crystals, m.p. 168–169 °C (Found: C, 51.8; H, 5.45. $C_8H_{10}O_3S$ requires C, 51.6; H, 5.4%); ν_{max}/cm^{-1} 1313, 1296, 1214, 1167, 1135, 1110, 1050, 990, 945, 911, 898, 791, 770, 726 and 714; δ_H 6.37 (2 H, d, J 1), 4.73 (2 H, d, J 1), 3.4–3.2 (2 H, m) and 2.85–2.4 (4 H, m); m/z 187 (M^+, 0.05%), 121 (0.7), 120 (1.4), 107 (1.1), 91 (2), 79 (1.5), 77 (3), 69 (5) and 68 (100, furan).

Flash Vacuum Pyrolysis of Unsaturated Sulfones **5–8**.—The general techniques and apparatus used have been described previously.[31] The products from small-scale pyrolyses were dissolved in $CDCl_3$ and analysed directly by ^1H NMR spectroscopy and/or GLC while the products from larger scale preparative pyrolyses were isolated, purified and characterised in the normal way. The pyrolysis conditions are given as follows: (weight of compound pyrolysed, furnace temperature, mean pressure during pyrolysis, inlet temperature).

(a) *Compound* **5**. Pyrolysis of **5** (45 mg, 850 °C, 5 × 10^{-3} mmHg, 50–80 °C) gave unchanged **5** (5 mg), insoluble polymeric material (6 mg) and a yellow liquid. Analysis of this

by NMR and GLC showed it to consist of a 70% yield (based on reacted starting material) of hydrocarbons, made up of benzene (33%), toluene (28%) and five minor components (total 8%).

(b) *Compound* **6**. Pyrolysis of **6** (92 mg, 675 °C, 1×10^{-3} mmHg, 60–120 °C) gave unchanged **6** (5 mg), polymeric material (25 mg) and a yellow liquid. Elemental analysis showed that the polymer approximated very closely to a 1:1 copolymer of cyclopentadiene and SO_2 (Found: C, 45.0; H, 4.7. Calc. for $C_5H_6O_2S$: C, 46.1; H, 4.6%). Analysis of the liquid (NMR) showed the presence of cyclopentadiene and buta-1,3-diene. The yields, including the cyclopentadiene in the polymer, were 42 and 34%, respectively on the reacted **6**.

(c) *Compound* **7**. Pyrolysis of **7** (120 mg, 750 °C, 2×10^{-3} mmHg, 50–100 °C) gave unchanged **7** (5 mg), a white 1:1 copolymer of cyclohexa-1,3-diene and SO_2 (20 mg) (Found: C, 49.1; H, 5.1. Calc. for $C_6H_8O_2S$: C, 50.0; H, 5.6%) and a yellow liquid containing cyclohexa-1,3-diene and benzene. Including the cyclohexadiene in the polymer, the yields were 60 and 20%, respectively, on reacted **7**.

(d) *Compound* **8**. Pyrolysis of **8** (50 mg, 675 °C, 5×10^{-3} mmHg, 70–100 °C) gave polymer (2 mg) and a yellow liquid which contained furan and buta-1,3-diene in 72 and 51% yield, respectively, from **8**.

Pyrolysis of Epoxy Sulfones.—The preparation of compounds **18**–**21** was described in a previous report.[32]

(a) *Compound* **18**. Pyrolysis of **18** (0.5 g, 725 °C, 10^{-3} mmHg, 70–100 °C) followed by microdistillation gave a colourless liquid. Analysis by GLC and GLC–MS showed the presence of seven compounds of which two were identified as *o*-xylene and styrene and two had *m/z* 124 corresponding to the expected (*Z*)- and (*E*)-4,5-epoxyocta-1,7-diene (*cis*- and *trans*-diallyloxiranes); δ_H 6.1–5.5 (2 H, m); δ_C 136.90, 133.42, 130.45, 118.66, 117.13, and 115.15 (3 vinyl groups), 55.67 (CH), 47.67, 41.26, 32.15 and 27.52 (all CH_2).

(b) *Compound* **19**. Pyrolysis of **19** (0.5 g, 700 °C, 4×10^{-3} mmHg, 150–160 °C) followed by microdistillation gave 2,4-*divinyl*-6-*oxabicyclo*[3.1.0]*hexane* **16** (0.13 g, 39%) (Found: M^+, 136.0880. $C_9H_{12}O$ requires M^+, 136.0888); ν_{max}/cm^{-1} 3085, 1745 (C=O impurity), 1640, 995, 917 and 844; δ_H 5.9–5.6 (2 H, m), 5.2–4.9 (4 H, m), 3.42 (2 H, s), 3.0–2.8 (2 H, m) and 2.0–1.3 (2 H, m); δ_C 138.7, 115.6, 60.4, 42.9 and 33.6; *m/z* 136 (M^+, 21%), 121 (10), 118 (10), 107 (16), 100 (29), 94 (39) and 79 (100).

(c) *Compound* **20**. Pyrolysis of **20** (94 mg, 700 °C, 2×10^{-3} mmHg, 140–160 °C) followed by microdistillation gave a colourless liquid (24.0 mg) which gave NMR signals corresponding to the expected 2,5-divinyl-7-oxabicyclo[4.1.0]-heptane; δ_H 6.1–5.6 (2 H, m), 5.25–4.85 (4 H, m), 3.1–2.4 (4 H, m) and 2.0–1.8 (4 H, m); δ_C 210.25 (C=O impurity), 140.52, 138.82, 137.77, 135.77, 135.56, 116.77, 115.64, 115.56 and 114.46 (4 vinyl groups), 55.40, 53.71, 47.11, 41.26 and 37.24 (all CH), 44.60, 29.43, 29.19, 27.86 and 22.14 (all CH_2).

(d) *Compound* **21**. Pyrolysis of **21** (0.5 g, 700 °C, 2×10^{-3} mmHg, 150–200 °C) followed by microdistillation gave 2,4-*divinyl*-3,6-*dioxabicyclo*[3.1.0]*hexane* **17** (0.21 g, 61%) as a colourless liquid (Found: M^+, 138.0675. $C_8H_{12}O_2$ requires M^+, 138.0681); ν_{max}/cm^{-1} 1423, 1054, 1036, 935, 866, 832 and 762; δ_H 6.0–5.5 (2 H, m), 5.5–5.2 (4 H, m), 4.59 (2 H, d, *J* 7) and 3.66 (2 H, s); δ_C 135.4, 118.2, 79.4 and 59.4; *m/z* 138 (M^+, 1%), 137 (1), 109 (8), 100 (44), 81 (45) and 55 (100).

Pyrolysis of Aziridines.—The preparation of compounds **25**, **26** and **27** was described in a previous report.[33]

(a) *Compound* **25**. Pyrolysis of **25** (34 mg, 725 °C, 2×10^{-3} mmHg, 100–120 °C) resulted in extensive decomposition with 12 mg residual tar in the inlet tube. NMR and GLC of the volatile products showed a complex mixture of compounds in which only ethanol could be identified.

(b) *Compound* **26**. Pyrolysis of **26** (37 mg, 675 °C, 2×10^{-3} mmHg, 140–150 °C) gave a yellow oil containing at least 13 components. Analysis by GLC–MS and NMR allowed identification of ethanol, ethyl carbamate, *o*-xylene and indene.

(c) *Compound* **27**. Pyrolysis of **27** (29 mg, 725 °C, 5×10^{-3} mmHg, 160–190 °C) gave an oil which contained 14 components. Only four of these could be identified: ethanol, ethyl carbamate, benzene and styrene.

Preparation of Sulfones **28**, **30**–**32** *and* **10**.—(a) cis-8-*Thiabicyclo*[4.3.0]*nonane* 8,8-*dioxide* **28**. A solution of sulfone **5** (0.365 g, 2.1 mmol) in dry ethanol (15 cm^3) was hydrogenated using 10% Pd on charcoal as catalyst at room temperature over 2 h. Evaporation gave the product as an oil which crystallised on storage and was recrystallised from Et_2O–hexane to give the title sulfone **28** (0.303 g, 82%) as colourless needles, m.p. 38–40 °C (lit.,[34] 39–41 °C); ν_{max}(melt)/cm^{-1} 2930, 2858, 1453, 1413, 1304, 1218, 1134, 1114, 912, 793 and 748; δ_H 3.18–2.91 (4 H, m), 2.68–2.41 (2 H, m) and 1.74–1.27 (8 H, m); δ_C 56.1 (CH_2), 36.1 (CH), 26.4 (CH_2) and 21.9 (CH_2); *m/z* 174 (M^+, 35%), 157 (63), 99 (74), 95 (18), 81 (26) and 67 (100).

(b) cis-8-*Thiabicyclo*[4.3.0]*nona*-1,3-*diene* 8,8-*dioxide* **30** *and* 8-*thiabicyclo*[4.3.0]*nona*-2,4-*diene* 8,8-*dioxide* **31**. (i) trans-3,4-*Dibromo*-cis-8-*thiabicyclo*[4.3.0]*nonane* 8,8-*dioxide* **29**. A solution of sulfone **5** (2.90 g, 16.9 mmol) in CH_2Cl_2 (15 cm^3) was stirred at −78 °C while bromine (3.29 g, 20.6 mmol) in CH_2Cl_2 (3 cm^3) was added dropwise over 20 min. After a further 30 min at −78 °C the mixture was allowed to warm to room temperature and evaporated. Recrystallisation of the residue from propan-2-ol gave the *title dibromo compound* **29** (5.26 g, 94%) as colourless needles, m.p. 190–192 °C (Found: C, 29.1; H, 3.7. $C_8H_{12}Br_2O_2S$ requires C, 28.9; H, 3.6%); ν_{max}/cm^{-1} 1293, 1249, 1221, 1200, 1122, 1078, 1004, 966, 877, 771, 733 and 679; δ_H 4.57–4.18 (2 H, m), 3.74–3.48 (1 H, m) and 3.28–1.90 (9 H, m); δ_C 57.9, 55.8, 53.4, 51.5, 37.3, 36.9, 36.5 and 36.1; *m/z* (M^+, 334/332/330 not apparent) 270 (7%), 268 (14), 266 (7), 253 and 251 (each 40, M^+ − Br), 189 (32), 187 (40), 171 (42), 107 (90), 105 (100) and 91 (58).

(ii) A suspension of dibromo compound **29** (11.48 g, 34.6 mmol) in dry THF was stirred at room temperature under N_2 while a solution of 1,8-diazabicyclo[5.4.0]undecane (DBU) (17.0 g, 113 mmol) in dry THF (45 cm^3) was added dropwise over 40 min. The mixture was stirred at 45 °C for 48 h and then added to water (40 cm^3). Extraction with CH_2Cl_2 (4×80 cm^3) followed by washing of the combined extracts with HCl (0.1 mol dm^{-3}; 5×50 cm^3), saturated aqueous NaCl (50 cm^3), water (50 cm^3), and then drying and evaporation gave a brown oil (4.75 g). This was purified by medium-pressure liquid chromatography on silica using light petroleum (b.p. 40–60 °C)–Et_2O to give two products.

At R_f 0.39 a colourless oil was obtained which crystallised on cooling to −20 °C and was recrystallised from diisopropyl ether to give cis-8-*thiabicyclo*[4.3.0]*nona*-2,4-*diene* 8,8-*dioxide* **31** (2.70 g, 46%) as colourless flakes, m.p. 35–36.5 °C (Found: C, 56.3; H, 5.9. $C_8H_{10}O_2S$ requires C, 56.4; H, 5.9%); $\lambda_{max}(Et_2O)$/nm 264 (ε/dm^3 mol^{-1} cm^{-1} 3640), 274 (3240); ν_{max}(melt)/cm^{-1} 3400, 2948, 1407, 1371, 1303, 1217, 1123, 978, 867, 786, 757, 698 and 645; δ_H 6.03–5.79 (2 H, m), 5.69–5.46 (2 H, m) and 3.28–2.92 (6 H, m); δ_C 126.0, 124.8, 54.9 and 34.4; *m/z* 170 (M^+, 32%), 105 (38), 104 (25), 92 (26), 91 (100), 79 (16), 78 (47) and 77 (14).

At R_f 0.29 a solid was obtained which was recrystallised from diisopropyl ether to give 8-*thiabicyclo*[4.3.0]*nona*-1,3-*diene* 8,8-*dioxide* **30** (0.61 g, 10%) as colourless needles, m.p. 112–113.5 °C (Found: C, 56.3; H, 5.7. $C_8H_{10}O_2S$ requires C, 56.4; H, 5.9%); ν_{max}/cm^{-1} 1628, 1578, 1427, 1276, 1239, 1226, 1188, 1150, 1127, 1099, 853 and 810; δ_H 6.33–6.31 (2 H, m), 6.22 (1 H, d, *J* 2), 3.52–3.43 (1 H, m), 3.24–3.06 (1 H, m), 2.94–2.84 (1 H, m), 2.38–

2.31 (2 H, m), 2.15–2.03 (1 H, m) and 1.60–1.39 (1 H, m); δ_C 148.6 (4ry), 140.1 (CH), 122.5 (CH), 121.5 (CH), 55.9 (CH_2), 36.4 (CH), 27.8 (CH_2) and 25.5 (CH_2); *m/z* 170 (M^+, 26%), 153 (17), 141 (40), 122 (26), 107 (72), 91 (100), 79 (90) and 77 (61).

(c) trans-8-*Thiabicyclo*[4.3.0]*nona*-2,4-*diene* 8,8-*dioxide* **32**. (i) *trans*-5,6-Bis(hydroxymethyl)cyclohexa-1,3-diene. A solution of *trans*-1,2-dihydrophthalic acid[21] (0.56 g, 3.33 mmol) in dry THF (10 cm^3) was added dropwise over 30 min to a stirred suspension of $LiAlH_4$ (0.36 g, 9.5 mmol) in dry THF under N_2. After the addition the mixture was heated under reflux for 3 h and then cooled and the excess $LiAlH_4$ destroyed by sequential addition of water (0.5 cm^3) in THF (3.5 cm^3), 15% aqueous NaOH (0.5 cm^3) and finally water (0.5 cm^3). The resulting mixture was filtered and the solid washed well with THF and CH_2Cl_2 and the combined filtrate and washings were evaporated to dryness. The residue was taken up in CH_2Cl_2 (20 cm^3) which was dried and evaporated to give the title diol (0.35 g, 75%) as a light yellow oil; ν_{max}/cm^{-1} 3650–3000br (OH), 2925, 2872, 1459, 1413, 1367, 1202, 1025, 952 and 696; δ_H 6.08–5.82 (2 H, m), 5.75–5.48 (2 H, m), 3.79–3.46 (4 H, m) and 2.80–2.27 (4 H, m); δ_C 126.0, 124.3, 64.5 and 38.4; *m/z* 140 (M^+, 7%), 122 (22), 120 (27), 107 (25), 104 (18), 93 (72), 92 (87), 91 (90) and 79 (100). This was used without further purification for preparation of the bis(toluene-*p*-sulfonate).

(ii) trans-5,6-*Bis*(p-*tolylsulfonyloxymethyl*)*cyclohexa*-1,3-*diene*. A solution of the diol from (i) (0.28 g, 2.0 mmol) in pyridine (10 cm^3) was added dropwise over 50 min to a solution of toluene-*p*-sulfonyl chloride (2.32 g, 12.2 mmol) in pyridine (10 cm^3) stirred at 0 °C. After the addition the mixture was stirred at 0 °C for a further 3 h and then added to ice–water (100 cm^3). Careful acidification by addition of hydrochloric acid (1 mol dm^{-3}) led to precipitation of the product which was filtered off, washed well with water and vacuum dried. Recrystallisation from CH_2Cl_2–propan-2-ol gave the *title bis*(*toluene*-p-*sulfonate*) (0.47 g, 52%) as colourless flakes, m.p. 101–101.5 °C (decomp.) (Found: C, 58.8; H, 5.4. $C_{22}H_{24}O_6S_2$ requires C, 58.9; H, 5.4%); ν_{max}/cm^{-1} 1596, 1357, 1189, 1166, 1097, 941, 837, 812, 699 and 664; δ_H 7.74 and 7.33 (8 H, A_2B_2 pattern, *J* 8), 6.02–5.79 (2 H, m), 5.57–5.28 (2 H, m), 3.98–3.75 (4 H, m) and 2.78–2.39 (8 H), m); δ_C 144.7 (2 C, 4ry), 132.8 (2 C, 4ry), 129.7 (4 C), 127.7 (4 C), 125.6 (2 C), 122.9 (2 C), 68.4 (2 C), 33.3 (2 C) and 21.4 (2 C); *m/z* (M^+, 448 not apparent) 173 (22%), 172 (100), 155 (27), 108 (43), 107 (84), 106 (36) and 91 (96).

(iii) *trans*-8-Thiabicyclo[4.3.0]nona-2,4-diene. Following the literature procedure by Paquette and Houser,[22] a stirred mixture of sodium sulfate nonahydrate (13.2 g, 55 mmol) and hexamethylphosphoramide (50 cm^3) was dehydrated by distillation at 25 mmHg until the stillhead temperature reached 125 °C. The resulting deep blue solution was cooled to room temperature and the bis(toluene-*p*-sulfonate) from (ii) (5.0 g, 11.0 mmol) was added. After being stirred for 24 h, the mixture was added to water (100 cm^3) and extracted with Et_2O (4 × 200 cm^3). The extracts were washed with water (3 × 150 cm^3), dried and evaporated, and the residue distilled to afford crude title sulfide as a colourless oil (1.0 g) which contained some benzyl methyl sulfide. This was used without further purification for oxidation to the sulfone.

(iv) trans-8-*Thiabicyclo*[4.3.0]*nona*-2,4-*diene* 8,8-*dioxide* **32**. A solution of the above sulfide (0.47 g, 3.37 mmol) in dry Et_2O (10 cm^3) was stirred at 0 °C while a solution of *m*-chloroperoxybenzoic acid ('85%', 1.46 g, 7.2 mmol) in dry Et_2O (30 cm^3) was added dropwise over 1 h. The mixture was then stirred at room temperature for 44 h before being washed with an excess of saturated aqueous Na_2CO_3, dried and evaporated. Preparative TLC (silica, Et_2O) of the residue followed by recrystallisation of the major component from CH_2Cl_2–diisopropyl ether gave the *title sulfone* **32** [0.24 g, 27% from bis(toluene-*p*-sulfonate)] as colourless needles, m.p. 129–132 °C (Found: C, 56.8; H, 6.0. $C_8H_{10}O_2S$ requires C, 56.4; H, 5.9%); $\lambda_{max}(Et_2O)/nm$ 258 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 1275); ν_{max}/cm^{-1} 1412, 1318, 1296, 1234, 1176, 1114, 1035, 897, 781 and 683; δ_H 6.17–5.75 (4 H, m) and 3.41–2.72 (6 H, m); δ_C 126.6 (CH), 126.3 (CH), 56.6 (CH_2) and 38.8 (CH); *m/z* 170 (M^+, 15%), 105 (35), 104 (23), 91 (100), 78 (20) and 65 (22).

(d) *Conversion of sulfone* **31** *into sulfone* **10**. A solution of sulfone **31** (85 mg, 0.5 mmol) in dry benzene (5 cm^3) containing 10% Pd on charcoal (150 mg) was heated under reflux under nitrogen for 15 h. The solution was filtered and evaporated to give a crystalline residue which was recrystallised from $CHCl_3$–diisopropyl ether to afford 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide **10** (55%) as colourless crystals, m.p. 149–150 °C (lit.,[35] 150–152 °C) identical with a sample prepared by the literature method.[11]

Pyrolysis of Sulfones **28** *and* **30**–**32**.—(a) *Compound* **28**. Pyrolysis of **28** (28 mg, 850 °C, 5 × 10^{-3} mmHg, 70 °C) gave insoluble polymeric material (2 mg), and a colourless liquid. Analysis of this by NMR and GLC showed it to consist of unchanged **28** (3.6 mg), octa-1,7-diene (41% yield based on reacted starting material), benzene (2%), butadiene and two further unidentified components.

Pyrolysis of **28** (54 mg, 925 °C, 5 × 10^{-3} mmHg, 75 °C) gave insoluble polymeric material (11 mg), and a colourless liquid. Analysis of this by NMR and GLC showed the absence of unchanged **28** and the presence of octa-1,7-diene (20% yield), benzene (3%), butadiene and two further unidentified components.

(b) *Compound* **30**. Pyrolysis of **30** (33 mg, 850 °C, 7 × 10^{-3} mmHg, 130 °C) gave a colourless solid and a yellow liquid which were shown by NMR and GLC to be unchanged **30** (52% recovery) and a mixture of styrene (21% yield), toluene (7%), ethylbenzene (1.5%), *o*-xylene (1.5%), benzene (0.5%) and two unidentified components (*ca.* 4%).

Pyrolysis of **30** (39 mg, 900 °C, 5 × 10^{-3} mmHg, 140 °C) gave a similar product to that above consisting of unchanged **30** (17%), toluene (17%), styrene (16%), benzene (6%), ethylbenzene (4.5%), *o*-xylene (1.5%) and two unidentified components (*ca.* 3.5%).

Pyrolysis of **30** (38 mg, 950 °C, 5 × 10^{-3} mmHg, 150 °C) gave a similar product to that above consisting of unchanged **30** (2%), styrene (37%), toluene (35%), benzene (11%), ethylbenzene (5%), *o*-xylene (0.5%) and two unidentified components (*ca.* 2%).

(c) *Compound* **31**. Pyrolysis of **31** (44 mg, 850 °C, 3 × 10^{-3} mmHg, 140 °C) gave a yellow oil which was shown by NMR and GLC to be unchanged **31** (15% recovery) and a mixture of benzene (50% yield based on reacted **31**), styrene (11%), ethylbenzene (8%), *o*-xylene (5%), toluene (3%) and two unidentified components (*ca.* 2%).

(d) *Compound* **32**. Pyrolysis of **32** (3 mg, 650 °C, 4 × 10^{-3} mmHg, 90 °C) gave a yellow oil which was shown by NMR, GLC and GC–MS to be a mixture of a compound of formula C_8H_{10} (65% yield), *o*-xylene (14%), benzocyclobutene (4%) and styrene (2%). The major product was tentatively identified on the basis of its ^1H NMR and mass spectra to be an 85:15 equilibrium mixture of cycloocta-1,3,5-triene **33** and bicyclo-[4.2.0]octa-2,4-diene **34**; *m/z* (GC–MS) 106 (M^+, 54%), 105 (24), 91 (100), 79 (21), 78 (43), 77 (22), 65 (20), 51 (26) and 39 (32).

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