Intramolecular nucleophilic interception by the sulfonyl group of reaction intermediates arising from electrophilic addition to unsaturated non-conjugated bicyclic sulfones

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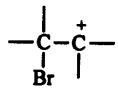
Electrophilic addition of molecular bromine and related reactions to unsaturated bicyclic sulfones resulting in atypical addition is described. Bromination of the bicyclic sulfone 3 results in a *ca.* 1:1 mixture of *exo,exo*- and *exo,endo*-dibromides 4 and 5, respectively. Similarly, acid-catalysed cleavage of epoxide 8 produces a 37:63 mixture of *exo,exo*- and *exo,endo*-bromohydrins 9 and 10, respectively. In both cases, formation of *exo,exo*-products is explained in terms of a favourable stabilising effect, which can be quenched by the presence of water in the reaction media, between the polar SO_2 group and the incipient carbocation centre as depicted in 6. Also described is formal nucleophilic neighbouring group participation by the *endo*-sited sulfonyl group in norbornylene systems 12 which leads exclusively to the *exo,exo*-dibromides 13 upon ionic bromination. In the case of unsaturated sulfone 27, bromination to form the *exo,exo*-dibromide 30 occurs *via* decomposition of an isolable, albeit metastable, tribromide salt 29. Owing to a similar effect, treatment of the related *exo*-epoxide 16 with hydrogen bromide in acetic acid results in the regio- and stereo-specific formation of *exo*-bromohydrin 17 as the sole product.

Intramolecular nucleophilicity has been reported for a variety of polar functional groups including carboxyl,[1] ester[2] and nitro[3] moieties. In particular, the sulfinyl group is well known to undergo many intramolecular nucleophilic reactions,[2,4] but similar nucleophilic behaviour by the oxygen atoms of the sulfonyl group had not been recognised until we reported briefly the first examples, involving capture by a sterically favourable sulfone grouping of reaction intermediates from the electrophilic addition of molecular bromine and related reactions to unsaturated bicyclic sulfones.[5] These exploratory studies are now reported in detail and evidence is also presented for an unprecedented electrophilic stereoselection by means of a remote sulfonyl group, even though the geometry of the olefin precludes transannular participation. Preliminary results of these findings have also been reported.[6]

Sixty years ago, Roberts and Kimball[7] pointed out that the stereochemistry of the addition of molecular bromine to a carbon–carbon double bond was incompatible with the formation of an intermediate carbocation **1** and suggested that an intermediate bromonium ion **2** was formed in which the bromine used one of its unshared pairs of electrons to bond to both carbon atoms of the double bond. This made rotation about the C–C bond in **2** impossible, and by necessity involved Br^- attack from the backside to give *anti*-addition as was observed.



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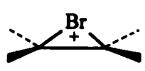

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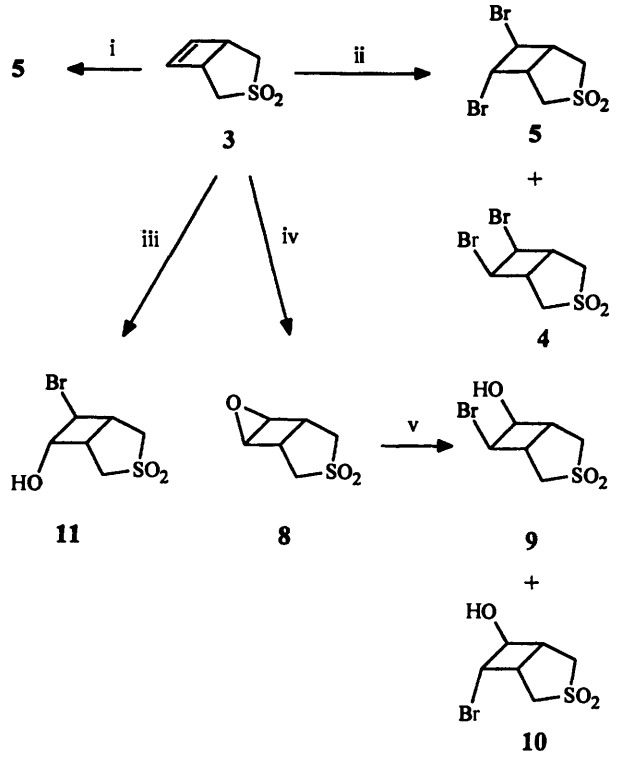
In general, the bromonium ion concept rationalises the *trans*-stereochemistry of bromine additions satisfactorily, with the proviso that those alkenes which can form highly stabilised carbocations, or where molecular rearrangements can occur, need not form such a structure. Exceptions to the bromonium ion rule include addition to conjugated dienes[8] in which the intermediate carbocation can be resonance-stabilised, norbornene systems[9] which can undergo Wagner–Meerwein δ-bond shifts and norbornadienes[10] which although are non-conjugated can give rise to π-shifts to form nortricyclic structures. Other notable exceptions can arise from transannular participation and include the stereospecific *cis*-bromination of a norbornenyl system brought about by an *endo*-nitro group,[3] and the formation of a *cis*-dibromide (albeit as a 30:70 mixture with its *trans*-isomer) from Dewar benzene through double bond participation without a skeletal rearrangement.[11]

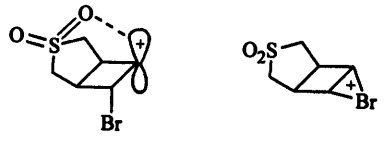
We have previously reported the preparation and utility of the bicyclic sulfone **3** as a masked form of *cis*-hex-1,3,5-triene.[12] In the present context and in contrast to other non-conjugated alkenes, **3** behaved differently towards ionic bromine addition. The reaction proceeded sluggishly to give a quantitative 1:1 mixture (by NMR spectroscopy) of isomeric *exo,exo*- and *exo,endo*-dibromides **4** and **5**, respectively (Scheme 1). That the mixture represented a kinetically controlled product distribution was established by separation of the isomers by flash chromatography and subsequent confirmation of their stability to the reaction conditions. Their stereochemical arrangement was established by ^{13}C NMR spectroscopy which showed a three-line spectrum for the symmetrical *exo,exo*-dibromide **4** and a six-line spectrum for the unsymmetrical *exo,endo*-dibromide **5**. Since ionic *syn*-addition of bromine to a non-conjugated cyclic alkene is rare, an X-ray diffraction study was carried out to validate the *exo,exo* nature of the product **4**.[5]

Radical involvement in the formation of **4** and **5** was precluded on the basis of the sluggish nature of the reaction (which is infinitely slow at −78 °C), together with the normal precautions of carrying out the reaction in the dark, using an oxygen purge and control experiments using radical scavengers.

The formation of **4** at the expense of an equal amount of the expected *exo,endo*-product **5** requires the intermediacy of the open carbocation **6**, followed by the subsequent *syn*-attack by Br^- at a rate that is competitive with normal *anti*-collapse of the bromonium ion **7**. From an inspection of Dreiding models,



Scheme 1 *Reagents and conditions:* i, $(C_4H_9)_4N^+Br_3^-$, $CHCl_3$; ii, Br_2, dry $CHCl_3$, 34 °C; iii, $CH_3CONHBr$, acetone–H_2O (4:1); iv, 30% H_2O_2–90% HCO_2H, 50 °C; v, 45% HBr–glacial HOAc, 5 °C



there is no question that the SO_2 moiety can provide sufficient steric bias to divert the incoming Br^- away from the *anti*-face, hence causing the *syn*-attachment of two large bromine atoms. Also discounted was a formal neighbouring group participation by the sulfone group in the sense of a fully fledged intramolecular bonding participation. This is supported by X-ray evidence which shows that the distance of the *endo*-oxygen of the sulfone group is at least 3.23 Å distant from the double bond moiety in **3**. Furthermore, even if bonding could occur, it should lead to overall *syn*-addition, whereas in practice there is an equal preference for *anti*-addition. We proposed that the relaxation in the usual demand for bromonium ion formation followed by backside attack is brought about by an unprecedented favourable stabilising effect of a long-range Coulombic (orbital) interaction between the polar SO_2 group and the carbocation centre as depicted in **6**. Evidence for a long-range interaction of this nature can be supported on both physical and chemical grounds. We have already described[13] the π-ionisation potential ($E_{I,\pi}$ = 10.25 eV) of **3** as being significantly higher than that of the parent cyclobutene (9.43 eV), or for that matter, comparable sulfones where the SO_2 group is remote from the double bond. This is believed to be a direct consequence of orbital interactions both through-space and through-bond between the sulfonyl group and the double bond, making the latter electron deficient. Chemically, this in turn would account for the sluggish nature in the progression of the bromination, and also why **3** fails to react with ethoxycarbonylnitrene under homogeneous conditions.[12]

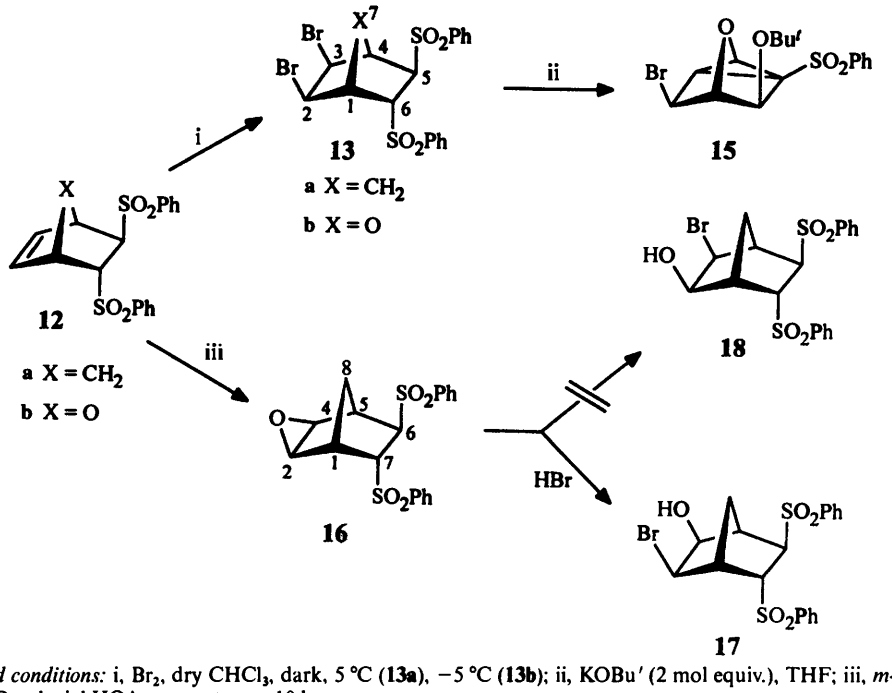
Bromination of alkenes is comparable in mechanistic terms to acid cleavage of the corresponding epoxide which normally proceeds with *trans*-stereochemistry.[14] To investigate this phenomenon further, the sulfone **3** was converted into its epoxide **8** having a *transoid*-configuration as shown by NOE studies, and treated with hydrogen bromide in acetic acid. The reaction proceeded quantitatively to furnish a 37:63 mixture (by NMR spectroscopy) of the *exo,exo*- and *exo,endo*-bromohydrins **9** and **10**, respectively. Attempts to separate these isomers by chromatography was frustrated by their decomposition, but the stereochemical assignments were confirmed from coupling constants and by an NOE study. This stereochemical outcome is in keeping with the formation of both *exo,exo*- and *exo,endo*-isomers from the bromination of **3** and can be similarly explained by invoking the intermediacy of an open carbocation whose formation is brought about by the stabilising effect of the SO_2 group on the carbocation centre, followed by *syn*-attack by the incoming nucleophile (Br^-).

Contrary to the acid-catalysed ring-opening of epoxide **8**, the corresponding reaction of alkene **3** with *N*-bromoacetamide in aqueous acetone or *N*-bromosuccinimide in aqueous *tert*-butyl alcohol, both of which are synthetic equivalents of hypobromous acid (HOBr), resulted in the sole formation of the *exo,endo*-bromohydrin **11** in 62% yield. By virtue of previous arguments, it had been anticipated that the aforementioned reactions would have again furnished an isomeric mixture of *exo,exo*- and *exo,endo*-bromohydrins. This seemingly anomalous behaviour can be explained in terms of the quenching of the sulfonyl group's stereochemical directing properties by solvation with water in the reaction medium. This explanation also served to account for the failure of **3** to react with ethoxycarbonylnitrene under homogeneous conditions, whereas under phase-transfer conditions the expected *N*-ethoxycarbonylaziridine was satisfactorily formed.[12]

In order to test this hypothesis further, the bromination of **3** was repeated in both wet and dry 1,2-dimethyoxyethane (DME). Under dry conditions, the reaction proceeded as before to give a *exo,exo*- and *exo,endo*-isomeric mixture of **4** and **5**, but in aqueous DME, bromination of **3** gave the *exo,endo*-isomer only. This would seem to confirm that the presence of water in the reaction medium does indeed suppress the sulfone group's ability to influence the stereochemical course of the aforesaid reactions.

Organic tribromide salts like pyridine hydrobromide perbromide (PHP) and tetrabutylammonium tribromide (TBAT) serve as synthetic equivalents for bromine in addition to carbon–carbon double bonds. On treatment with TBAT in chloroform, the alkene **3** yielded the *exo,endo*-dibromide **5** as the sole product in 71% yield. This behaviour corresponds to the bromination of both *cis*- and *trans*-stilbenes which with PHP give only the products of *anti*-addition[15] whereas molecular bromine leads to a mixture of *meso*- and (±)-dibromides.[16] Also, the addition of free bromine to buta-1,3-diene in chloroform gives mostly the 1,4-adduct, whereas PHP and TBAT yield almost exclusively the 1,2-dibromide.[17] These synthetically interesting differences on stereo- and regio-selectivity of free Br_2 and Br_3^- addition reactions clearly point to different mechanistic pathways. Bellucci *et al.*[18] have attributed such differences to the formation of a non-ionic transition state, in contrast to the bromonium ion–tribromide ion pair invoked for free bromine addition. This non-ionic transition state serves to explain the suppression of *syn*-addition to conjugated olefins and of 1,4-addition to dienes. It also accounts for the formation of a single *exo,endo*-isomer in the bromination of **3**.

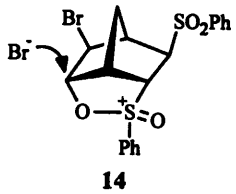
Next we turned our attention to compounds **12a**, **12b** where inherent flexibility in the norbornenyl ring system would allow the electrophilic reaction partner to be sited more favourably for intramolecular capture by the sulfonyl group in a truly transannular manner. Both compounds were prepared by the method of De Lucchi *et al.*[19] by the Diels–Alder reaction between cyclopentadiene and furan with (*E*)-1,2-bis(phenylsulfonyl)ethylene. In both cases ionic bromination resulted in the formation of the *exo,exo*-bromides **13a**, 89%; **13b**, 96% as the sole products (Scheme 2), the stereochemical



Scheme 2 *Reagents and conditions:* i, Br_2, dry $CHCl_3$, dark, 5 °C (**13a**), −5 °C (**13b**); ii, KOBu^t (2 mol equiv.), THF; iii, *m*-CPBA, CH_2Cl_2, room temp., 4 days; iv, 45% HBr–glacial HOAc, room temp., 10 h

assignment of which rested most convincingly on coupling constants in the ^{1}H NMR spectra. In the case of the methylene bridged compound **13a**, H-2 is the most deshielded at 5.32 ppm by virtue of being directly attached to a carbon bearing a bromine atom and also situated adjacent to the *endo*-phenylsulfonyl group. This appeared as a doublet of doublets with J = 6.8 and 2.0 Hz. The former is typical of a *cis*-coupling constant in these systems;[20] the latter is due to the long range W-coupling with H-7a, again well precedented[21] and indicative that H-2 is *endo*, particularly as *exo*-protons do not couple with bridging protons. This long-range coupling was of course not present in the oxo-bridged analogue. Also, the absence of coupling between protons H-2, H-3 with the bridgehead protons H-1 and H-4, respectively, is further proof that the *cis*-protons are *endo*. This phenomenon is well documented[22,23] and can be understood on the basis of the Karplus rule.

This result is striking in that complete *exo,exo*-bromination was achieved, particularly in view of the fact that the *exo,endo*-dichloro- and -dicyano-alkene analogues of **12a** both undergo stereospecific *anti*-addition of bromine under ionic conditions.[19,22] In order to account for the stereospecific *syn*-addition of bromine to alkenes **12a,b** we must invoke a formal intramolecular nucleophilic neighbouring group participation by the sulfonyl group. An inspection of Dreiding models for these systems reveals that the sulfonyl oxygen atom is only 1.92 Å away from the olefinic centre, so rendering a bonding situation entirely feasible. In effect, an initially formed bromonium ion is deemed to be captured by the SO_2 moiety of the *endo*-phenylsulfonyl group to give the intermediate **14**, which then suffers attack by the incoming Br^- from the normally hindered *exo*-direction.



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Chemical evidence which further substantiates the *exo,exo*-dibromo stereochemistry of **13a,b** was realised when the oxo-bridged dibromide **13b** was treated with 2 equiv. of potassium *tert*-butoxide in tetrahydrofuran (THF). This gave the nortricyclic compound **15** in 67% yield due to the elimination of HBr and displacement of $PhSO_2$ by the base. Previous evidence for such a γ-elimination has been reported by Payo *et al.*[1] in the formation of an analogous nortricyclic system from *exo*-2, *endo*-3-dibromo-*exo,exo*-5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptane using sodium methoxide as base. For this elimination to be successful it seems clear that the stereochemistry must be of a desired orientation, namely that there be an α-*endo* proton and a γ-*exo* leaving group.

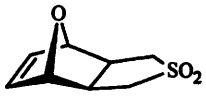
Oxidation of **12a** with *m*-chloroperoxybenzoic acid (*m*-CPBA) gave the *exo*-epoxide **16** in almost quantitative yield. The *exo*-nature of the oxirane ring was established by the same methods as employed for the *exo,exo*-dibromide **13a**. Namely, the *cis*-coupling constant between H-2 and H-4, the long-range coupling between H-2, H-4 and the bridging proton H-8a and the absence of any coupling between H-2 and H-4 with the bridgehead protons H-1 and H-5, respectively. All other couplings were consistent with the proposed structure.

The reaction of this epoxide with hydrogen bromide in acetic acid resulted in the formation of the *exo*-bromohydrin **17** in 70% yield as the sole product. The stereochemistry of **17** was determined from H–H coupling constants and double resonance studies. In particular, the bridgehead proton H-1 appears as a doublet of doublets at 2.98 ppm with J = 4.0 Hz due to the coupling with *exo*-H-6 and J = 1.8 Hz from the long-range W-coupling to the other bridgehead proton H-4 which appears as a discrete doublet at 2.62 ppm (J = 1.8 Hz). H-2 appears as a doublet of doublets at 5.29 ppm with J = 6.0 Hz, the *cis* coupling to H-3, and J = 2.0 Hz from the long-range coupling to H-7a. H-3 appears as a multiplet at 3.81 ppm with identical couplings to H-2 with the exception of an additional coupling of 4.8 Hz to the hydroxy proton. However, even after the detailed assignment of all signals on the basis of couplings and coupling constants, it could not be ruled out that the structure could in fact be the isomeric *cis*-bromohydrin **18** and not the proposed structure **17**. Clarification of this point was obtained from an NOE study. From coupling constants, with respect to **17**, it was known that H-1 is on the same side of the ring as the *endo*-phenylsulfonyl group due to its coupling with H-6. Similarly, H-4 is on the same side of the ring as the *exo*-phenylsulfonyl group from the absence of any coupling to H-5. Thus irradiation at H-1 and H-4 should lead to enhancements of H-2, H-6 and H-3, H-5, respectively. This indeed proved to

be the case, so precluding the alternative isomer **18**. In addition, with respect to irradiation at H-4, an NOE was also seen from the *ortho* protons of the phenylsulfonyl group geminal to H-5 indicating its *exo*-nature.

The outcome of the aforementioned reaction, especially the fact that not only is the normally favoured *endo*-product absent, but that the actual product is a single stereo- and regio-specific isomer argues strongly for the intramolecular nucleophilic participation by the sulfonyl group.

In contrast to previous observations, the ionic addition of molecular bromine to the oxo-bridged sulfone **19**, prepared



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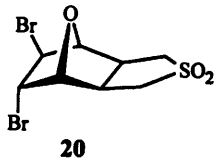

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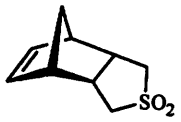

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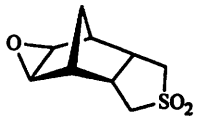

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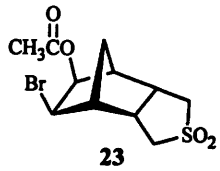

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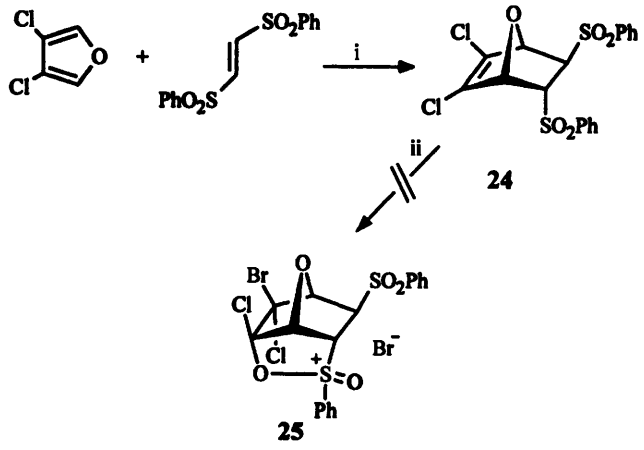
from the cycloadduct of furan and maleic anhydride by conventional methods,[24] resulted in *anti*-electrophilic addition. The unsymmetrical nature and hence *exo,endo*-stereochemistry of the product **20** was confirmed by the eight-line ^{13}C NMR spectrum. Since the olefin had *exo*-stereochemistry at the ring junction, the sulfonyl group is now some considerable distance from the double bond (5.8 Å). Therefore, in the absence of any stereoelectronic influence by the SO_2 group, the bromination proceeds predictably to give *anti*-addition.

The tricyclic sulfone **21** can be prepared in five steps by the method of Wilder and Felin-Otero[25] from cyclopentadiene and maleic anhydride. Oxidation of **21**, in which the SO_2 group is *endo* to the ring junction, with *m*-CPBA resulted in the formation of the *exo*-epoxide **22** in 72% yield.[13] Treatment of **22** with HBr in acetic acid gave the *exo*-8-bromo-*exo*-9-acetoxy compound **23** in 86% yield. Normally this reaction would yield the bromohydrin. However in this case, after the initial reaction had taken place, the reaction mixture was subjected to prolonged heating at 90 °C, thus effecting conversion into the α-bromoester. This heating had not taken place in previous examples. The *exo,exo*-nature of **23** was confirmed by the *cis*-coupling constant of $J = 6.0$ Hz between H-8 and H-9, the long-range couplings to the bridging proton H-10 and by the absence of any couplings between H-8, H-9 with the bridgehead protons H-1 and H-7, respectively. A large NOE was also observed between H-8 and H-9. There is of course the possibility that after initial bromoester formation the *O*-acyl or *O*-alkyl cleavage could take place. In the case of *O*-acyl cleavage, the stereochemistry of an initially formed bromohydrin must be retained showing that stereocontrol has been maintained. If, on the other hand, *O*-alkyl cleavage had taken place, then again we are observing stereocontrol, as attack on an open carbocation has resulted in the preferential *exo,exo*-attack by a bulky nucleophile next to a large bromine atom.

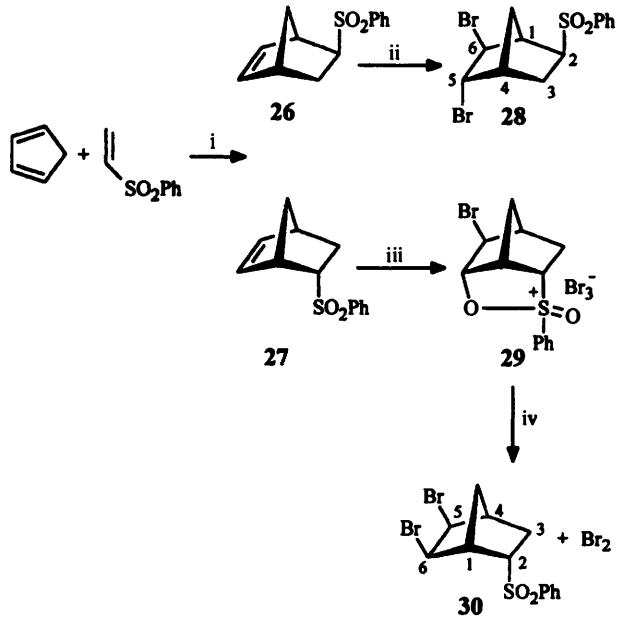
In an attempt to trap the intermediate involved in the previous reactions of electrophilic addition of bromine to norbornene systems containing an *endo*-phenylsulfonyl group, compound **24** was synthesised in 81% yield by the Diels–Alder cycloaddition of 3,4-dichlorofuran with (*E*)-1,2-bis(phenylsulfonyl)ethene (Scheme 3). The diene was prepared by the method of Mkryan *et al.*[26] in five steps from butyne-1,4-diol. It had been hoped that when the cycloadduct **24** was treated with



Scheme 3 *Reagents and conditions:* i, toluene, 95 °C, 14 h; ii, Br_2, $CHCl_3$, reflux

bromine, the initially formed bromonium ion would be captured by virtue of a nucleophilic neighbouring group participation by the SO_2 group and furnish the salt **25**, which should not now be susceptible to *exo*-attack by an incipient Br^- due to a steric blocking effect by the *exo*-chlorine atom. Unfortunately, no reaction took place on addition of bromine to a chloroform solution of **24** even after a protracted period at ambient temperature and a further period at reflux. This can only be attributed to the severe deactivation of the double bond by the electron-withdrawing chlorine and phenylsulfonyl substituents. The attempted epoxidation of **24** with *m*-CPBA was also unsuccessful, as was the treatment with HBr in acetic acid. The monophenylsulfonyl analogues of **24** were also prepared as a mixture of the *endo*- and *exo*-isomers by the reaction of 3,4-dichlorofuran with phenylvinylsulfone at 100 °C in toluene. However, once again, no reaction took place with either bromine or *m*-CPBA.

In a similar vein, cyclopentadiene was reacted with phenylvinylsulfone[28] at room temperature in benzene to give a mixture of *exo*- and *endo*-2-(phenylsulfonyl)bicyclo[2.2.1]hepta-5-enes **26** and **27**, respectively (Scheme 4). When a chloroform solution



Scheme 4 *Reagents and conditions:* i, benzene, room temp., 110 h; ii, Br_2 (1.1 mol equiv.), dry $CHCl_3$, 0 °C; iii, Br_2 (2 mol equiv.), dry $CHCl_3$, room temp.; iv, room temp., 5 days

of the *exo*-isomer **26** was treated with bromine at room temperature, instantaneous decolourisation took place. This is in direct contrast to the general observation of the sluggish

reaction progression where there is nucleophilic participation by the sulfonyl group. Indeed, this instantaneous decolourisation was expected because the phenylsulfonyl group is *exo* to the norbornene ring, thereby precluding any possibility of a nucleophilic neighbouring group participation by the sulfonyl group. One would predict three possible products from this reaction, these being two distinct *trans*-isomers arising from simple addition, and a Wagner–Meerwein rearrangement product. In practice, the reaction proceeded to give a single product **28** which was isolated in 87% yield. That a single isomer resulted from this reaction was evidenced from a single spot on tlc and the observation of seven aliphatic signals in the ^{13}C NMR spectrum of the crude reaction mixture. This product was positively identified as **28** from ^{1}H NMR double resonance and NOE experiments, in a manner similar to that described previously.

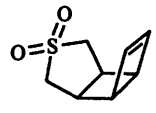
This result is somewhat surprising in that all three isomers seemed to be distinct possibilities. The rearrangement product would have been formed by a σ-migration of the C-3, C-4 carbon–carbon bond. From previously illustrated examples and literature citations[19,21] it was known that rearrangements are not observed when both positions on the opposite side of the ring from the double bond are occupied by electron-withdrawing substituents. However, in this case only one such position is occupied, so in theory this should leave the other positions (C-3–C-4) open to σ-migration. In practice, as no such rearrangement is observed, the driving force for the formation of **28** must be a more favoured process.

On steric grounds, with respect to simple *anti*-addition, a cyclic bromonium ion should be equally susceptible to posterior attack at either of the two possible *endo* positions. In turn, this would lead to a mixture of *trans*-isomers. As this is clearly not the case, there must in all likelihood be a tendency towards unequal charge distribution. The development of positive charge at the 5-position relative to the 6-position would appear to be a more favourable process owing to the presence of the electron-withdrawing phenylsulfonyl group at C-2. Although this is a somewhat long-range inductive effect, it is clearly powerful enough to effect the observed regio- and stereospecificity.

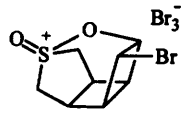
When a chloroform solution of the *endo*-isomer **27** was treated dropwise with 1.1 equiv. of bromine, this resulted in the almost immediate precipitation of an orange solid. Examination of the mother liquor by tlc showed that an appreciable amount of the starting material still remained. It was not until 2 equiv. of bromine had been added that tlc showed that all the starting material had been consumed. When left open to the atmosphere at room temperature for 60 h this material had largely decomposed to a colourless crystalline solid. When enclosed in a sample tube, the material was seen to release fumes of bromine after 24 h. Combustion analysis of the orange solid showed it to have the empirical formula $C_{13}H_{14}Br_4O_2S$. Also the melting point was uncharacteristically low at only 77 °C. Taken as a whole, these features of consumption of 2 equiv. of bromine, insolubility in organic media and a molecular formula consistent with a tetrabromide leads to the conclusion that we are observing an example of a 'captured bromonium ion' salt **29**. Indeed a Raman experiment, using an argon laser (457.9 nm) showed the appearance of a strong absorption band at 149 cm^{-1} corresponding to the Br_3^- counterion.[29] The IR spectra of sulfonyl systems invariably show two strong S=O stretching frequencies at 1320–1300 and 1150 cm^{-1}. However, in this case whilst there is a strong signal at 1300 cm^{-1}, the other signal appears at 1082 cm^{-1}. This would correspond to a weakening in the S–O bond strength and would be consistent with the reduced bond order for the oxygen atom participating in the intramolecular bonding. The ^{13}C NMR spectrum could at best be achieved as an 80:20 mixture with the decomposition product. Nonetheless, the resonances of the salt could be assigned readily on the basis of integral differences between the two materials. The ^{1}H NMR spectrum was obtained at 360 MHz within 15 min of preparation and clearly resolved the nine aliphatic and five aromatic protons pertaining to **29**. However, an NOE experiment carried out on **29** casts some doubt on the proposed stereochemistry, so precluding definitive characterisation.

As mentioned previously, this tribromide salt decomposed over 60 h to a colourless crystalline solid. This was identified as the *exo,exo*-dibromide **30**. The stereochemistry of this system was again determined from H–H coupling constants, double resonance and NOE studies. Of particular relevance was the *cis*-coupling constant of 6.8 Hz between H-5 and H-6 accompanied by a large NOE, a 2.1 Hz long-range coupling to bridging proton H-7 and the absence of any coupling to bridgehead protons H-1 and H-4.

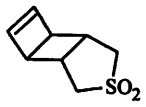
In concurrent bromination studies within these laboratories it has been shown that the *cisoid*-tricyclic sulfone **31** undergoes a similar reaction to **27** to give the bromothiadecanylium tribromide **32**.[5] On the other hand, the *transoid*-isomer **33** undergoes instantaneous decolourisation to yield the *trans*-dibromide **34** only, as was the case with **26**. In both these situations the sulfonyl group is spacially situated in an unfavourable position to effect nucleophilic participation. Full details of these studies will be reported in a later publication.



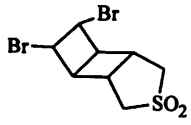
31



32



33



34

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. IR spectra were recorded for Nujol mulls on a Perkin-Elmer spectrophotometer. ^{1}H NMR spectra were recorded at 200 MHz on a Bruker WP-200 instrument or at 360 MHz on a Bruker WH360 instrument and ^{13}C NMR spectra were recorded at 90 MHz on a Bruker WH360 instrument. Spectra were obtained for solutions in $CDCl_3$ unless otherwise indicated with Me_4Si as internal standard. Coupling constants *J* are given in Hz; c m refers to a complex multiplet. Mass spectra were obtained on an AEI MS902 instrument using electron impact at 70 eV. Raman spectra were obtained on an Annaspace 33 Laser Raman Spectrometer using 457.9 nm excitation from a Spectra Physics Model 171 argon ion laser.

exo,exo- and *exo,endo*-6,7-Dibromo-3-thiabicyclo[3.2.0]heptane-3,3-dioxide 4 and 5

To a solution of **3**[12] (2.837 g, 19.7 mmol) in 20 ml of dry chloroform was added dropwise with stirring in the dark, a solution of dry bromine (3.36 g, 21.0 mmol) in 5 ml of dry chloroform. The reaction mixture was maintained at 34 °C while the bromine was added over 2 h, after which time the reaction mixture had turned pale orange with a white precipitate. The reaction mixture was stirred for a further 1 h, followed by chilling in an ice bath and subsequent filtration of the precipitate (4.6 g, 77%). This was subjected to flash chromatography over silica gel using

hexane–diethyl ether as eluent to give as the first fraction after recrystallisation from ethanol the title *cis*-dibromo compound **4** as colourless microneedles, mp 168–170 °C (Found: C, 23.50; H, 2.36. $C_6H_8Br_2O_2S$ requires C, 23.70; H, 2.65%); ν_{max}/cm^{-1} 1300 (SO_2) and 1145 (SO_2); δ_H(200 MHz, $CDCl_3$), 3.19–3.22 (4 H, m, C-2-H and C-4-H), 3.67–3.72 (2 H, m, C-1-H and C-5-H), 4.86–4.90 (2 H, d of d, *J* 1.4 and 4.1, C-6-H and C-7-H); (NOE) irrd C-6-H, C-7-H, 0% enhancement; irrd C-1-H, C-5-H, 0% enhancement; δ_C(50 MHz, DEPT 3π/4, $CDCl_3$) 43.30, 48.54, 53.39; δ_C(50 MHz, DEPT 3π/4, [$^2H_6$]acetone) 42.94, 49.19, 51.87; *m/z* 305 (M^+, 1%), 306 (0.5), 304 (0.5), 225 (84), 223 (81), 188 (8), 184 (15), 161 (59), 159 (177), 121 (86), 119 (100); crystal data: $M = 304.01$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.430$, $b = 6.650$, $c = 12.723$, $\beta = 91.2°$, $V = 882$ Å^3, $Z = 4$, $D_c = 2.29$ g cm^{-3}, $F(0,0,0) = 584$, (Mo-K) = 92.8 cm^{-1}, $R = 0.042$, $R = 0.047$ for 1366 reflections. The second fraction after recrystallisation from ethanol gave the title *trans*-dibromo compound **5** as colourless rhombic crystals, mp 160–163 °C (Found: C, 23.44; H, 2.56. $C_6H_8Br_2O_2S$ requires C, 23.70; H, 2.65%); ν_{max}/cm^{-1} 1305 (SO_2) and 1140 (SO_2); δ_H(200 MHz, $CDCl_3$) 3.19–3.75 (6 H, c m, C-1-H, C-2-H, C-4-H and C-5-H), 4.56–4.63 (1 H, t, *J* 8 and 8, C-7-H), 4.76–4.84 (1 H, t, *J* 8 and 8, C-6-H); δ_C(50 MHz, DEPT 3π/4, $CDCl_3$) 39.45, 42.28, 49.32, 52.03, 54.17; *m/z* 225 (100%), 223 (96), 188 (12), 184 (20), 161 (68), 159 (76), 121 (76), 119 (80).

***transoid*-8-Oxa-4-thiatricyclo[5.1.0.0^{2,6}]octane-4,4′-dioxide 8**

Sulfone **3** (2.5 g, 17.3 mmol) was added portionwise over 0.5 h to a mixture of 12 ml of 30% hydrogen peroxide in 50 ml of 90% formic acid at room temperature. The reaction mixture was stirred at 50 °C for 48 h, followed by a further 48 h at room temperature. The solvent was then evaporated and the residual oil taken up in a small amount of ethanol. This was left in the ice box overnight after which time the product had crystallised. Recrystallisation from diisopropyl ether gave the title epoxide **8** (1.24 g, 44.7%) as colourless crystals, mp 118–119 °C (Found: C, 44.78; H, 5.00. $C_6H_8O_3S$ requires C, 44.99; H, 5.03%); δ_H(200 MHz, $CDCl_3$) 2.85–2.90 (2 H, m, C-6-H and C-2-H), 3.09–3.21 (4 H, c m, C-3-H and C-5-H), 3.88–3.91 (2 H, d, *J* 2, C-7-H and C-1-H; (NOE) irrd C-1-H, C-7-H, 2% enhancement on C-3-H, C-5-H *endo* protons; irrd C-2-H, C-6-H, 6% enhancement on C-3-H and C-5-H *exo*-protons; irrd C-3-H, C-5-H *endo* protons, 12% enhancement on C-3-H and C-5-H *exo* protons and 3% on C-1-H and C-7-H; irrd C-3-H, C-5-H *exo* protons, 11% enhancement on C-3-H and C-5-H *endo* protons and 5% on C-2-H and C-6-H; δ_C(50 MHz, DEPT 3π/4, $CDCl_3$) 40.77, 49.57, 64.43; *m/z* 159 (M^+, 13%), 135 (6), 131 (6), 119 (17), 104 (30), 103 (23), 95 (97), 94 (100).

***exo,exo*- and *endo,exo*-6-Bromo-7-hydroxy-3-thiabicyclo[3.2.0]-heptane-3,3′-dioxide 9 and 10**

To a solution of **8** (0.10 g, 0.62 mmol) in 1 ml of glacial acetic acid at −10 °C, was added, dropwise with stirring, a solution of 45% hydrogen bromide in glacial acetic acid (0.053 g, 0.65 mmol) over 15 min. The reaction mixture was allowed to stir at 5 °C for a further 3 h, followed by evaporation of the solvent at the oil pump. Subsequent preparative tlc of the reaction mixture over silica resulted in the decomposition of the products. However, ^{13}C, ^1H NMR and ^1H (NOE) spectroscopy clearly indicated the presence of the two isomers, **9** and **10**. **9**: δ_H(360 MHz, [$^2H_6$]acetone) 3.10–3.45 (6 H, c m, C-1-H, C-2-H, C-4-H and C-5-H) 4.49–4.53 (1 H, t, *J* 7 and 7.5, C-7-H), 4.58–4.62 (1 H, t, *J* 7.5, C-6-H); (NOE) irrd C-6-H and C-7-H signals are too close to irradiate without perturbation of the other signal; δ_C(50 MHz, DEPT 3π/4, [$^2H_6$]acetone) 33.04, 40.14, 48.87, 51.72, 53.57, 78.56. **10**: δ_H(360 MHz, [$^2H_6$]acetone) 3.20–3.65 (6 H, c m, C-1-H, C-2-H, C-4-H and C-5-H), 4.87–4.92 (1 H, d of d, *J* 7.5 and 8.8, C-7-H), 5.27–5.32 (1 H, t of d, *J* 7.5, 7.5 and 1.1, C-6-H); (NOE) irrd C-6-H, 0% enhancement on C-7-H; irrd C-7-H, 0% enhancement on C-6-H; δ_C(50 MHz, DEPT 3π/4, [$^2H_6$]acetone) 34.45, 38.48, 43.72, 51.23, 53.16, 78.36.

***exo*-6-Bromo-*endo*-7-hydroxy-3-thiabicyclo[3.2.0]heptane-3,3′dioxide 11**

To a solution of **3** (0.20 g, 1.39 mmol) in 5 ml of 4:1 acetone–water, was added, dropwise over 15 mins, a solution of *N*-bromoacetamide (0.211 g, 1.5 mmol) in acetone. The reaction mixture was stirred at room temperature for 20 h. The solution was evaporated and the residue taken up in 20 ml of water, followed by extraction with methylene chloride (3 × 20 ml). The combined organic extracts were washed successively with saturated aqueous $NaHCO_3$, water and brine, followed by drying and evaporation of the solvent. The residue was triturated with chloroform. The resulting colourless solid was recrystallised from ethanol–chloroform to give the title compound **11** as colourless crystals, mp 140–143 °C (Found: C, 29.10; H, 3.63. $C_6H_9BrO_3S$ requires C, 29.89; H, 3.76%); ν_{max}/cm^{-1} 3440 (O–H), 1290 (SO_2) and 1140 (SO_2); δ_H(200 MHz, [$^2H_6$]acetone) 3.05–3.63 (6 H, c m, C-1-H), 4.55–4.59 (1 H, d of d, *J* 0.6 and 7, C-7-H); δ_C(50 MHz, DEPT 3π/4, [$^2H_6$]toluene) 36.22, 39.39, 47.18, 51.01, 52.20, 71.78; *m/z* 242 (M^+, 25%), 222 (25), 160 (90), 158 (100), 146 (30), 144 (45), 133 (35), 131 (35), 119 (60), 117 (55) (Exact *m/z*: Found 241.9436. $C_6H_9BrO_3S$ requires 241.9437).

***endo*-6,*exo*-7-Dibromo-3-thiabicyclo[3.2.0]heptane-3,3′-dioxide 5**

To a solution of tetrabutylammonium tribromide (2.625 g, 0.54 mmol) in 5 ml of chloroform was added compound **3** (72 mg, 0.5 mmol) in one portion. The reaction mixture was stirred at room temperature for 2 h, after which time tlc showed that all the starting material had reacted. The reaction mixture was washed successively with aqueous sodium thiosulfate, water and brine. After separation the organic phase was dried and evaporated to give a pale yellow solid. This was recrystallised from ethanol to give the title compound **5** (80 mg, 53%) as colourless crystals, mp 159–163 °C; ν_{max}/cm^{-1} (SO_2) and 1140 (SO_2). Fingerprint region identical to that of the *trans*-dibromide received from direct bromination (*vide supra*).

***exo,exo*-2,3-Dibromo-*exo*-5-*endo*-6-bis(phenylsulfonyl)bicyclo-[2.2.1]heptane 13a**

To a solution of **12a**[19] (0.374 g, 1.0 mmol) in 15 ml of dry chloroform at 0 °C was added a solution of dry bromine (0.176 g, 1.1 mmol) in 5 ml of dry chloroform, dropwise over 0.5 h, in the dark. The reaction mixture was stirred overnight at 5 °C, followed by washing with 5% aqueous sodium thiosulfate and brine. The organic phase was then dried and evaporated *in vacuo* to give a solid residue which was recrystallised from ethanol to give the title compound **13a** (0.51 g, 96%) as colourless crystals, mp 215–216.5 °C (Found: C, 42.50; H, 3.31. $C_{19}H_{18}Br_2O_4S_2$ requires C, 42.71; H, 3.39%); ν_{max}/cm^{-1} 1315 (SO_2) and 1150 (SO_2); δ_H(200 MHz, CD_2Cl_2) 2.08–2.16 (1 H, d of t, *J* 2.0 and 11.5, C-7-H), 2.38–2.46 (1 H, d of q, *J* 2.0 and 11.5, C-7-H), 3.01–3.04 (2 H, q, *J* 1.5 and 4.8, C-1-H and C-4-H), 3.61–3.68 (1 H, d of d, *J* 2.0 and 5.5, C-5-H), 4.10–4.15 (1 H, m, *J* 4.8 and 5.5, C-6-H), 4.34–4.38 (1 H, d of d, *J* 2.0 and 6.8, C-3-H), 5.30–5.35 (1 H, d of d, *J* 2.0 and 6.8, C-2-H), 7.55–7.96 (10 H, c m, Ar Hs); δ_C(50 MHz, DEPT 3π/4, CD_2Cl_2) 33.95, 51.34, 52.95, 53.21, 65.49, 66.07, 128.64, 128.79, 129.86, 129.94, 134.88; *m/z* 537 (10%), 535 (M^+, 22), 533 (10), 455 (100), 453 (95), 440 (15), 393 (52), 385 (15), 348 (20), 339 (45), 311 (37), 277 (15), 261 (25), 251 (30).

***exo,exo*-2,3,Dibromo-*exo*-5-*endo*-6-bis(phenylsulfonyl)-7-oxabicyclo[2.2.1]heptane 13b**

To a solution of **12b**[19] (0.188 g, 0.50 mmol) in 10 ml of dry chloroform at −5 °C was added a solution of dry bromine (0.90 g, 0.56 mmol) in 10 ml of dry chloroform over 45 mins, in

the dark. The reaction mixture was stirred for a further 1 h at −5 °C. The reaction mixture was then washed successively with (1 × 25 ml) of 5% aqueous sodium thiosulfate and brine, followed by drying and evaporation of the solvent. The solid residue was recrystallised from ethanol to give the title compound **13b** (0.237 g, 89%) as colourless crystals, mp 265–266.5 °C (Found: C, 40.48; H, 2.98. $C_{18}H_{16}Br_2O_2S_2$ requires C, 40.31; H, 3.01%); ν_{max}/cm^{-1} 1318 (SO_2) and 1147 (SO_2); δ_H(200 MHz, CD_2Cl_2) 3.80–3.82 (1 H, d, *J* 5.0, C-5-H), 4.12–4.17 (1 H, t, *J* 5.0 and 6.0, C-6-H), 4.51–4.54 (1 H, d, *J* 7.0, C-3-H), 4.93–4.96 (1 H, d of d, *J* 2.0 and 6.0, C-1-H), 5.12–5.13 (1 H, d, *J* 2.0, C-4-H), 5.34–5.37 (1 H, d, *J* 7.0, C-2-H), 7.53–7.93 (10 H, c m, Ar Hs); δ_C(50 MHz, DEPT 3π/4, [$^2H_6$]DMSO) 50.75, 52.09, 65.18, 65.92, 85.50, 88.07, 128.05, 128.45, 129.48, 129.63, 134.54, 134.84; *m/z* 536 (M^+, 10%), 456 (10), 454 (9), 438 (42), 436 (40), 315 (100), 251 (8), 235 (13), 208 (38).

exo-2-*tert*-Butoxy-*exo*-3-phenylsulfonyl-*exo*-6-bromo-7-oxatricyclo[2.2.1.0^{3,5}]heptane 15

To a solution of potassium *tert*-butoxide (50 mg, 0.45 mmol) in 10 ml of dry THF under an atmosphere of dry nitrogen was added **13b** (117 mg, 0.22 mmol). The solution turned brown almost immediately. This was stirred at room temperature under nitrogen overnight. The solvent was then evaporated *in vacuo* and the residue taken up in 20 ml of methylene chloride. The organic phase was washed with 2 × 15 ml of water and 1 × 15 ml of brine prior to drying and evaporation of the solvent. Dry flash chromatography was used to separate the product from some polar material. Recrystallisation of the solid from chloroform gave the title compound **15** as colourless rhombic crystals, mp 166–167 °C (Found: C, 49.62; H, 4.84. $C_{16}H_{19}BrO_4S$ requires C, 49.62; H, 4.94%); ν_{max}/cm^{-1} 1308 (SO_2) and 1150 (SO_2); δ_H(200 MHz, $CDCl_3$) 1.02 [9 H, s, $(CH_3)_3$], 2.96–2.99 (1 H, d of t, *J* 1.3 and 4.0, C-5-H), 4.08 (1 H, s, C-2-H), 4.12–4.13 (1 H, d, *J* 1.3, C-4-H), 4.18 (1 H, s, C-2-H), 4.78–4.80 (1 H, d, *J* 4.0, C-6-H), 7.47–7.93 (5 H, c m, C_6H_5); δ_C(50 MHz, $CDCl_3$) 27.77, 29.30, 43.40, 48.30 (quat. C), 59.11, 71.94, 75.30 (quat. C), 81.42, 128.11, 128.71, 133.37, 140.59 (quat. C); *m/z* 389 (M^+, 4.8%), 387 (4.2), 332 (100), 330 (100), 308 (9), 286 (24), 284 (24), 253 (76), 216 (70), 181 (42).

exo-3-Oxa-*exo*-6,*endo*-7-bis(phenylsulfonyl)tricyclo[3.2.1.0^{2,4}]-octane 16

To a solution of **12a**[19] (0.50 g, 1.33 mmol) in 10 ml of dry methylene chloride was added a solution of *m*-chloroperoxybenzoic acid (0.288 g, 80%) in 10 ml of dry methylene chloride. The reaction mixture was stirred for four days at room temperature, then filtered and washed successively with 2 × 25 ml of 6% aqueous sodium hydroxide and 2 × 25 ml of brine, followed by drying and evaporation of the solvent. The crude product was recrystallised from ethanol–chloroform to give the title epoxide **15** (0.530 g, 97%) as colourless crystals, mp 203–205 °C; ν_{max}/cm^{-1} 1305 (SO_2), 1150 (SO_2) and 1220 (C–O); δ_H(200 MHz, $CDCl_3$) 1.44–1.45 (1 H, d, *J* 11, C-8-H), 1.55–1.61(1 H, d of d, *J* 1.8 and 11, C-8-H), 2.95–2.96 (1 H, d, *J* 1.5, C-5-H), 3.02–3.05 (1 H, d of d, *J* 1.5 and 3.5, C-1-H), 3.22–3.25 (1 H, d of d, *J* 1.5 and 3.5, C-4-H), 3.59–3.63 (1 H, d of d, *J* 1.8 and 5.5, C-6-H), 3.87–3.88 (1 H, d, *J* 3.5, C-2-H), 4.11–4.16 (1 H, d of d, *J* 3.5 and 5.5, C-7-H), 7.24–7.92 (10 H, c m, Ar Hs); δ_C(50 MHz, DEPT 3π/4, $CDCl_3$) 24.38, 41.48, 41.76, 48.64, 49.31, 63.98, 68.21, 128.19, 128.34, 129.20, 129.37, 134.08, 134.18; *m/z* 391 (M^+, 0.8%), 331 (1.2), 309 (1.5), 266 (2.4), 265 (13), 250 (11), 248 (13), 247 (26), 157 (11), 127 (7), 126 (16), 125 (100), 107 (46) (Exact *m/z*: Found 390.0566. $C_{19}H_{18}O_5S_2$ requires 390.0591).

exo-2-Bromo-*exo*-3-hydroxy-*exo*-5,*endo*-6-bis(phenylsulfonyl)-bicyclo[2.2.1]heptane 17

To a partial suspension of **16** (0.20 g, 0.51 mmol) in 15 ml of glacial acetic acid was added, dropwise with stirring, a solution of 45% hydrogen bromide in glacial acetic acid (0.104 g, 1.3 mmol) in 5 ml of glacial acetic acid. After 0.5 h no undissolved solid remained. The reaction mixture was then allowed to stir at room temperature for 10 h. The solvent was then evaporated at the oil pump. The solid residue was recrystallised from ethanol to give the title compound **17** (0.167 g, 70%) as colourless crystals, mp 199–200 °C; ν_{max}/cm^{-1} 3260 (OH), 1308 (SO_2) and 1152 (SO_2); δ_H(200 MHz, $CDCl_3$) 1.95–2.06 (1 H, d of d, *J* 2 and 12, C-7-H), 2.12–2.20 (1 H, d of d, *J* 1.7 and 12, C-7-H), 2.25–2.27 (1 H, d, *J* 4.8, OH), 2.62–2.63 (1 H, d, *J* 1.8, C-4-H), 2.97–3.00 (1 H, d of d, *J* 1.8 and 4, C-1-H), 3.52–3.55 (1 H, d of d, *J* 1.7 and 5.7, C-5-H), 3.78–3.84 (1 H, m, *J* 2, 4.8 and 6, C-3-H), 4.06–4.11 (1 H, d of d, *J* 4 and 5.7, C-6-H), 5.27–5.32 (1 H, d of d, *J* 2 and 6, C-2-H); (NOE) irrd C-1-H, enhancement on C-6-H and C-2-H; irrd C-4-H, enhancement on C-3-H, C-5-H and *ortho* aromatic protons of *exo*-phenylsulfonyl group; δ_C(50 MHz, $CDCl_3$) 32.71, 49.32, 55.74, 64.19, 65.27, 71.87, 128.42, 129.31, 129.46, 134.40, 137.87, 138.70; *m/z* 472 (M^+, 5%), 470 (3), 419 (12), 391 (3), 332 (42), 330 (33), 311 (51), 249 (70), 233 (32), 189 (15), 143 (100), 125 (29), 107 (38) (Exact *m/z*: Found 471.9825. $C_{19}H_{19}BrO_5S_2$ requires 471.9838).

endo-8,*exo*-9-Dibromo-10-oxa-*exo*-4-thiatricyclo[5.2.1.0^{2,6}]-decane-4,4′-dioxide 20

To a solution of **19**[24] (0.50 g, 2.69 mmol) dissolved in 35 ml of dry chloroform at 38 °C was added a solution of dry bromine (0.473 g, 2.9 mmol) in 15 ml of dry chloroform, dropwise with stirring over 2 h. The reaction mixture was stirred overnight at 38 °C, followed by washing with aqueous sodium thiosulfate and brine. The organic phase was then dried and evaporated to give a colourless solid. This was then recrystallised from ethanol to give the title compound **20** (0.529 g, 57%) as colourless crystals, mp 232–233 °C (decomp.) (Found: C, 29.77; H, 2.92. $C_8H_{10}Br_2O_3S$ requires C, 29.77; H, 2.91%); ν_{max}/cm^{-1} 1308 (SO_2) and 1155 (SO_2); δ_H(200 MHz, [$^2H_6$]DMSO) 2.67–2.98 (4 H, c m, C-3-H and C-5-H), 3.18–3.51 (2 H, m C-2-H and C-6-H), 4.42–4.61 (4 H, m, C-1-H, C-7-H, C-8-H and C-9-H); δ_C(50 MHz, [$^2H_6$]DMSO) 30.61, 37.49, 40.73, 50.89, 51.18, 54.10, 82.84, 87.51; *m/z* 349 (5%), 347 (M^+, 5), 345 (5), 239 (70), 2221 (13), 202 (37), 185 (100), 171 (82), 145 (18), 129 (34), 120 (39).

exo-8-Bromo-*exo*-9-acetoxy-*endo*-4-thiatricyclo[5.2.1.0^{2,6}]-decane-4,4′-dioxide 23

To a solution of *exo*-9-oxa-*endo*-4-thiatetracyclo[5.2.1.0^{2,6}0^{8,10}]-undecane-4,4′-dioxide **22**[13] (0.50 g, 2.7 mmol) in 30 ml of glacial acetic acid, was added a solution of 45% hydrogen bromide (0.22 g, 2.7 mmol) in glacial acetic acid, dropwise with stirring over 20 min. The reaction mixture was then stirred at 35 °C for 24 h, followed by rotoevaporation of the solvent. The residue was taken up in 25 ml of water and extracted with 2 × 25 ml of methylene chloride. The combined organic extracts were then washed with aqueous $NaHCO_3$ and brine prior to drying and evaporation of the solvent. Recrystallisation from ethanol–chloroform gave the title compound **23** as colourless crystals, mp 214–215 °C (Found: C, 40.40; H, 4.64. $C_9H_{13}BrO_3S$ requires C, 40.84; H, 4.68%); δ_H(200 MHz, $CDCl_3$) 1.55–1.61 (1 H, d, *J* 11, C-10-H), 2.10 (3 H, s, CH_3), 2.31–2.37 (1 H, d of d, *J* 1.5 and 11, C-10-H), 2.47–3.09 (8 H, c m, C-1-H, C-2-H, C-3-H, C-5-H, C-6-H and C-7-H); 4.39–4.44 (1 H, d of d, *J* 2.5 and 6, C-9-H), 4.91–4.95 (1 H, d of d, *J* 1.5 and 6, C-8-H); δ_C(50 MHz, $CDCl_3$) 20.70, 36.17, 37.78, 45.02, 48.71, 49,01, 49.43, 49.51, 50.48, 70.18, 169.80; *m/z* 323 (M^+, 1%) 280 (4), 265 (3), 264 (5), 254 (4), 201 (82), 146 (26), 144 (28), 121 (7), 119 (13), 91 (100).

2,3-Dichloro-*endo*-5,*exo*-6-bis(phenylsulfonyl)-7-oxabicyclo-[2.2.1]hept-2-ene 24

3,4-Dichlorofuran[26] (0.30 g, 2.19 mmol) and (*E*)-1,2-bis(phenylsulfonyl)ethylene (0.308 g, 1.0 mmol) together with 3 ml of

toluene were combined in a sealed tube.[27] This was then heated in an oil bath at 95 °C for 14 h, after which time tlc showed that none of the dienophile remained. The solvent was evaporated to give a colourless solid which was then recrystallised from light petroleum (40–60 °C)–chloroform to give the title compound **24** (0.362 g, 81%) as colourless crystals, mp 213–215 °C (Found: C, 48.2; H, 3.09. $C_{18}H_{14}Cl_2O_5S_2$ requires C, 48.5; H, 3.17%); ν_{max}/cm^{-1} 1615 (C=C), 1315 (SO_2) and 1150 (SO_2); δ_H(200 MHz, $CDCl_3$) 3.74–3.80 (1 H, d, *J* 4.5, C-5-H), 4.31–4.42 (1 H, t, *J* 4 and 4.5, C-6-H), 5.05–5.12 (1 H, d of d, *J* 1.5 and 4.0, C-1-H), 5.23–5.25 (1 H, d, *J* 1.5, C-4-H), 7.35–7.94 (10 H, c m, C_6H_5); δ_C(50 MHz, $CDCl_3$) 66.44, 83.58, 85.68, 128.43, 128.54, 129.47, 132.88 (quat. C), 134.11 (quat. C), 134.52, 137.44 (quat. C), 138.46 (quat. C); *m/z* 445 (M^+, 1%), 443 (1), 308 (16), 305 (25), 303 (31), 167 (19), 141 (69), 138 (40), 136 (62), 125 (100).

exo- and *endo*-5-(Phenylsulfonyl)bicyclo[2.2.1]hept-2-ene 26 and 27

Following the literature procedure of Maccagnani *et al.*,[28] to a solution of freshly distilled cyclopentadiene (0.863 g, 13.3 mmol) in 2 ml of benzene was added phenyl vinyl sulfone (2.0 g, 11.9 mmol). The resulting mixture was stirred at room temperature for 110 h after which time tlc showed that no starting material remained. The isomeric mixture was separated by flash chromatography over silica gel using light petroleum (40–60 °C) as eluent to give as the first fraction *exo*-5-(phenylsulfonyl)-bicyclo[2.2.1]hept-2-ene **26** (0.483 g, 16%) as colourless crystals, mp 62–63 °C (from chloroform–hexane) (lit.,[28] 64–65 °C); ν_{max}/cm^{-1} 1310 (SO_2) and 1045 (SO_2); δ_H(200 MHz, $CDCl_3$), 1.31–1.40 (1 H, m, C-6-H), 1.31–1.41 (2 H, m, C-6-H and C-7-H), 1.89–1.93 (1 H, br d, *J* 8.6, C-7-H), 2.03–2.13 (1 H, m, *J* 12.3, 4.7 and 3.5, C-6-H), 2.83–2.90 (1 H, m, *J* 7.5, 4.7 and 1.6, C-5-H), 3.18 (1 H, br s, C-1-H), 3.19 (1 H, br s, C-4-H), 6.01–6.05 (1 H, d of d, *J* 5.6 and 3.1, C-2-H), 6.17–6.21 (1 H, d of d, *J* 5.6 and 2.9, C-3-H), 7.25–7.97 (5 H, c m, ArHs); δ_C(50 MHz, DEPT 3π/4, $CDCl_3$) 28.33, 41.42, 44.28, 45.59, 64.14, 128.04, 129.04, 133.25, 135.24, 139,80; and as the second fraction *endo*-5-(phenylsulfonyl)bicyclo[2.2.1]hept-2-ene **27** (1.08 g, 39%) as colourless crystals, mp 67–68 °C (from hexane–ether) (lit.,[28] 66–67 °C); ν_{max}/cm^{-1} 1315 (SO_2) and 1048 SO_2; δ_H(200 MHz, $CDCl_3$) 1.20–1.24 (1 H, br d, *J* 8.6, C-7-H), 1.42–1.51 (1 H, c m, *J* 8.6, C-7-H), 1.52–1.61 (1 H, m, *J* 12.2, 5.1 and 2.5, C-6-H-*exo*), 1.92–2.05 (1 H, m, *J* 12.2, 9.2 and 3.7, C-6-H-*endo*), 2.98 (1 H, br s, C-1-H), 3.08 (1 H, br s, C-4-H), 3.55–3.64 (1 H, m, *J* 9.2, 5.1 and 3.2, C-5-H), 6.09–6.13 (1 H, d of d, *J* 5.7 and 2.8, C-2-H), 6.24–6.28 (1 H, d of d, *J* 5.7 and 3.1, C-3-H), 7.25–7.86 (5 H, c m, C_6H_5); δ_H(50 MHz, DEPT 3π/4, $CDCl_3$) 28.73, 42.61, 44.93, 64.70, 127.83, 128.99, 131.16, 133.15, 137.23.

exo-2-(Phenylsulfonyl)-*endo*-5-bromo-*exo*-6-bromobicyclo-[2.2.1]heptane 28

To a solution of **26** (95 mg, 0.406 mmol) in 3 ml of dry chloroform, was added dropwise with stirring in the dark at 0 °C, a solution of dry bromine (71 mg, 0.44 mmol) in 2 ml of dry chloroform. This resulted in instantaneous decolourisation. After addition, the reaction was complete as indicated by tlc. The reaction mixture was then washed with 5 ml portions of aqueous sodium thiosulfate and brine, prior to drying and evaporation of the solvent. Recrystallisation from chloroform–ethanol gave the title dibromo compound **28** (0.139 g, 87%) as colourless crystals, mp 156.5–157.5 °C (Found: C, 39.50; H, 3.54. $C_{13}H_{14}Br_2O_2S$ requires C, 39.62; H, 3.58%); ν_{max}/cm^{-1} 1300 (SO_2) and 1147 (SO_2); δ_H(200 MHz, $CDCl_3$) 1.99–2.27 (4 H, c m, C-3-H and C-7-H), 2.63–2.67 (1 H, m, C-4-H), 2.88 (1 H, br s, C-1-H), 3.01–3.09 (1 H, c t, C-2-H), 3.77–3.78 (1 H, t, C-6-H), 4.38–4.43 (1 H, m, C-5-H), 7.54–7.92 (5 H, c m, C_6H_5); ^1H NOE irrd *o*-Ph*H*, large C-1-H and C-2-H, small C-3-H; irrd C-5-H, large C-4-H, small C-6-H and C-7-H; irrd C-6-H, large C-1-H and C-2-H, small C-5-H; irrdn C-1-H, large C-6-H and *o*-Ph*H*; irrd C-4-H, large C-5-H and C-3-H; δ_C(50 MHz, DEPT 3π/4, $CDCl_3$) 27.10, 33.35, 44.21, 48.36, 57.17, 59.12, 63.55, 128.33, 129.41, 133.98; *m/z* 397 (5.1%), 395 (M^+, 9.8), 393 (5.1), 317 (5.4), 316 (13), 315 (100), 314 (14), 313 (92), 255 (5), 253 (9), 251 (6).

2-Bromo-4-oxa-5-oxo-5-phenyl-5-thiatricyclo[4.2.1.0^{3,7}]nonan-5-ylium tribromide 29

To a solution of **27** (40 mg, 0.17 mmol) in 0.5 ml of chloroform was added a solution of bromine (55 mg, 0.34 mmol) in 0.5 ml of chloroform. After a 3–4 drops of bromine had been added an orange precipitate was formed, and this continued to accumulate during the addition of the remainder of the bromine solution. The precipitate was filtered and washed with 1 ml of chloroform to give the title tribromide salt **29** (85 mg, 81%) as an orange solid, mp 77 °C (decomp.) (Found: C, 27.71; H, 2.45. $C_{13}H_{14}Br_4O_2S$ requires C, 28.19; H, 2.55%); ν_{max}/cm^{-1} 1570 (C=C), 1300 (S–O) and 1082 (S–O); δ_H(360 MHz, CD_3CN) 1.65–1.72 (1 H, d of d, *J* 9.8 and 13.8), 2.01–2.08 (1 H, br d of d, *J* 14.2 and 8.7), 2.09–2.14 (1 H, m, *J* 13.7, 6.4 and 4.7), 2.21–2.28 (1 H, d of t, *J* 14.2 and 4.5), 2.76 (1 H, br d), 2.81 (1 H, br d), 3.33–3.37 (1 H, d of d, *J* 9.8 and 6.2), 3.81–3.87 (1 H, br m), 4.47 (1 H, br s), 7.62–7.88 (5 H, C_6H_5); δ_C(50 MHz, DEPT 3π/4, $CDCl_3$) 30.81, 40.86, 44.95, 46.16, 49.41 (2), 62.60, 128.25, 129.44, 134.04.

endo-2-(Phenylsulfonyl)-*exo*-5,*exo*-6-dibromobicyclo[2.2.1]-heptane 30

A sample of the tribromide salt **29** was left open to the atmosphere for five days. After this time the orange salt had decomposed to an off-white crystalline solid. This was subsequently identified as the title dibromo compound **30** mp 142–143 °C (from ethanol); ν_{max}/cm^{-1} 1299 (SO_2) and 1148 (SO_2); δ_H(200 MHz, $CDCl_3$) 1.37–1.44 (1 H, d of d, *J* 11.1 and 1.6, C-7-H), 1.89–1.96 (2 H, m, C-3-H), 2.36–2.44 (1 H, br d, *J* 11.1, C-7-H), 2.73–2.76 (1 H, m, *J* 3.5 and 1.8, C-4-H), 2.80–2.82 (1 H, d of d, *J* 3.8 and 1.8, C-1-H), 3.34–3.44 (1 H, m, *J* 8.5 and 3.8, C-2-H), 4.43–4.47 (1 H, d of d, *J* 6.8 and 2.1, C-5-H), 5.37–5.41 (1 H, d of d, *J* 6.8 and 2.1, C-6-H), 7.53–7.90 (5 H, c m, ArHs); δ_C(50 MHz, DEPT, 3π/4, $CDCl_3$) 29.41, 35.66, 49.03, 50.56, 51.17, 55.40, 63.90, 127.71, 129.43, 133.93 (Exact *m/z*: Found 393.9058. $C_{13}H_{14}Br_2O_2S$ requires 393.9063).

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