SYNTHESIS AND FLASH VACUUM PYROLYSIS

OF CISOID- AND TRANSOID-

4-THIATRICYCLO[5.2.0.$0^{2,6}$]NON-8-ENE 4,4-DIOXIDE

AND DERIVED SYSTEMS

by

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VOLUME 2

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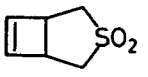
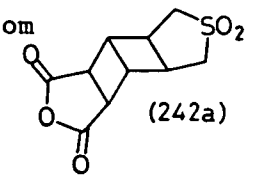
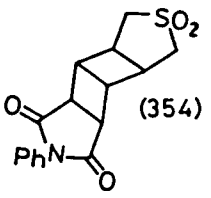
ii. Photolysis of  (63) with cyclic olefins

2. Preparation of tetracyclic systems from  (242a)

a. Preparation of  (354)

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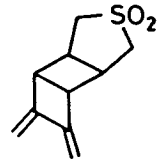
a. Preparation of  (374)

Symbols and Abbreviations

lit.	literature
mol; mmol	moles; millimoles
est.	estimated
M	mol dm^{-3}
h; min; sec	hours; minutes; seconds
GLC	gas-liquid chromatography
t_R	retention time
TLC	thin layer chromatography
R_f	R_f value
FVP	flash vacuum pyrolysis
VVP	vertical vacuum pyrolysis
MPLC	medium pressure liquid chromatography
GC-MS	gas chromatography-mass spectroscopy
m.p.; b.p.	melting point; boiling point
decomp.	decomposed
n^T_D	refractive index at temperature T(°C) and standard wavelength (sodium D line)
EA	elemental analysis
NMR	nuclear magnetic resonance
COSY	coupling correlated spectroscopy
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
DEPT	distortionless enhancement by polarisation transfer
Q	quaternary carbon atom
δ	chemical shift
ppm	parts per million
J	spin-spin coupling constant

s;d;t;q;m	singlet; doublet; triplet; quartet; multiplet
c;bd;sym;dist	complex; broad; symmetrical; distorted
IR	infrared
$\nu_{max.}$	maximum wave number
w, m_e, s	weak, medium, strong (intensity)
MS	mass spectroscopy
EI	electron impact
CI	chemical ionisation
FAB	fast atom bombardment
m/e	mass to charge ratio
M^+	molecular ion mass
UV	ultraviolet
$\lambda_{max.}$	maximum wavelength
$\epsilon_{max.}$	maximum extinction coefficient

Nomenclature

All compounds have been named, as far as possible, within the guidelines expressed by the IUPAC 1979 Rules, Sections A, B, C, D, E, F and H[219].

General Purification and Analytical Techniques

1. Purification and separation techniques

a. Drying and purification of solvents and gases

Commercially available solvents were used without further purification, unless otherwise indicated. Dry diethyl ether (referred to hereafter as ether), benzene and toluene were prepared by addition of sodium wire to the Analytical Reagent (A.R.) grade solvents. Dry methylene chloride and carbon tetrachloride were obtained by distillation from phosphorus pentoxide onto pre-dried molecular sieve. 'Superdry' methanol and ethanol were prepared by the method of Lund and Bjerrum, as described by Vogel[220], and stored over pre-dried molecular sieve. Dry pyridine was prepared by heating of this under reflux with potassium hydroxide for 2h followed by distillation of the fraction b.p. 114-117°C onto fresh potassium hydroxide pellets. Tetrahydrofuran was dried by heating A.R. grade solvent under reflux with CaH_2 in a dry nitrogen atmosphere for 2h, followed by distillation and storage over pre-dried molecular sieve.

Organic solutions obtained during work-up of reactions were dried by standing over anhydrous magnesium sulphate for several hours, followed by filtration. Removal of solvent from the resultant dried solutions was achieved by evaporation under reduced pressure on a Buchi rotary evaporator.

Dry nitrogen was obtained by passing the gas in turn through concentrated sulphuric acid, sodium hydroxide pellets, and calcium chloride granules.

b. Chromatographic separation techniques

i. Thin layer chromatography (TLC)

Analytical TLC was carried out using glass plates coated with 0.3 mm layers of silica (Merck, Kieselgel 60G) or alumina (Merck, neutral aluminium oxide 60G, Type E) incorporating 0.5% Woelm fluorescent green indicator. The components obtained on development of the plates were located by observation with UV light (λ = 254 nm), and by staining with iodine vapour.

Preparative TLC involved the use of plates coated with 1.0 mm thick layers of the above supports. After location of the separated bands as described above, the support was scraped from the plate and the purified products obtained by extraction of the support in 5% A.R. methanol in chloroform for 3h, followed by filtration, and then evaporation *in vacuo* of the filtrate.

ii. Column chromatography

Gravity columns (silica or alumina) were prepared using a minimum amount of packing of some seventy times the weight of the product mixture to be resolved, with packing of the column achieved by the slurry technique using either the initial eluant to be employed, or petroleum-ether, b.p. 40-60°C. For silica columns Fisons 'Silica Gel for chromatography (60-120 mesh)', appropriately deactivated, was employed; alumina columns were prepared using Laporte 'Alumina H (100-200 mesh)' deactivated by addition of either 6% or 10% (by weight) of water.

iii. Flash chromatography

The exact procedure described by Still *et al*[221] was adopted, this involving the application of a positive pressure (0.2-0.5 kg/cm^2)

of nitrogen gas to the solvent reservoir. Silica columns were prepared using Merck 'Kieselgel 60 (230-400 mesh)' silica.

iv. Medium pressure liquid chromatography (MPLC)

A standard MPLC apparatus incorporating a series II micrometering pump and a Budenburg pressure gauge was used. For small scale separations (ca 1g) a high performance liquid chromatography glass column (1m x 1.5 cm) containing Merck 'silica gel 60, for column chromatography' was employed; for larger scale separations (ca. 10g) a 1m x 2.5 cm silica column, with a appropriately sized pre-column, was utilised.

v. Gas-liquid chromatography (GLC)

Analytical GLC was carried out using a Philips PU 4500 chromatograph incorporating a flame ionisation detector. Glass columns (2m x 4.5 mm) containing 10% polyethyleneglycoladipate (PEGA), 5% and 10% carbowax 20M, and 5% silicon elastomer (SE 30), all on Chromosorb W (80-100 mesh) support, were used.

Preparative GLC was carried out using a Carlo Erba Strumentazione Fractovap 2450 instrument. Columns (0.85m x 12 mm) containing 10% and 30% PEGA on Chromosorb A (40-60 mesh) support were employed, the separated products being collected in dry ice/acetone cooled traps.

2. Analytical techniques

a. General analytical techniques

i. Melting point determinations

Routine melting points were determined using an Electrothermal melting point apparatus. The thermal behaviour, including melting

point determination, of novel compounds was studied using a Reichert hot-stage microscope. All melting points reported are uncorrected.

ii. Elemental analysis (EA)

The majority of microanalyses for carbon, hydrogen and nitrogen content were carried by Mr J. Grunbaum, University of Edinburgh, on a Perkin-Elmer 240 Elemental Analyser. A minor number of samples were analysed by the microanalytical staff of the Chemistry Department, University of St Andrews, and by staff of the Chemical Analysis Branch, BP Research Centre, Sunbury-on-Thames.

iii. X-Ray crystallography

An X-ray diffraction study was carried out by Dr R.M. Highcock, BP Research Centre, Sunbury-on-Thames, using an Enraf-Nonius CAD-4 diffractometer.

b. Spectroscopic techniques

i. Nuclear magnetic resonance (NMR) spectroscopy

Information from NMR spectra have been recorded in a format detailing: type of NMR spectroscopy used, the solvent and operating spectrometer frequency employed, together with chemical shift (δ) values (expressed in parts per million to high frequency of tetramethylsilane (TMS)), signal multiplicity, coupling constants and integral. The assignment of signals to nuclei has been made for a number of closely examined systems. The following NMR techniques and associated instrumentation were utilised:

α. ^{1}H NMR spectroscopy

Routine ^{1}H NMR spectra were obtained using a Varian EM-360 (60 MHz) spectrometer. Proton spectra of novel compounds, or of samples

requiring greater resolution, were obtained on Bruker WP-80-SY (80 MHz) or Bruker WP-200-SY (200 MHz) spectrometers operated by Mr L.H. Bell and Mr J.R.A. Millar respectively. High resolution ^{1}H NMR spectra were obtained on a Bruker WH-360 (360 MHz) spectrometer operated by Dr I.H. Sadler or Dr D. Reed. Selectively decoupled ^{1}H NMR spectra were obtained from the Bruker WP-200-SY and WH-360 spectrometers, with the latter instrument also the source of ^{1}H nuclear Overhauser effect (NOE) difference spectra.

A number of ^{1}H, ^{1}H-2D COSY (correlated spectroscopy) and ^{1}H-2D NOESY (nuclear Overhauser effect spectroscopy) analyses were provided by Dr J.R. Bales, Spectroscopy Branch, BP Research Centre, using a Bruker AM-250 (250 MHz) spectrometer.

β. ^{2}H NMR spectroscopy

Several broad-band decoupled ^{2}H NMR spectra were obtained using a Bruker WP-200-SY spectrometer (30.7 MHz) operated by Mr J.R.A. Millar.

γ. ^{13}C NMR spectroscopy

All ^{13}C NMR spectra reported refer to those determined following broad-band decoupling, unless otherwise indicated. ^{13}C NMR spectra for relatively large quantities of material were obtained on a Varian CFT-20 (25 MHz) spectrometer operated by Mr J.R.A. Millar or Ms E. Stevenson; for smaller quantities ^{13}C and ^{13}C DEPT (distortionless enhancement by polarisation transfer) NMR spectra were acquired on a Bruker WP-200-SY (50.3 MHz) or WH-360 (90.6 MHz) spectrometers operated by Mr J.R.A. Millar or Dr I.H. Sadler/Dr D. Reed, respectively.

A smaller number of ^{13}C, ^{13}C DEPT and 2D ^{13}C-^{1}H NMR spectra were obtained on a Bruker AM-250 (63.0 MHz) spectrometer operated by Dr J.R. Bales, BP Research Centre.

ii. Infrared (IR) spectroscopy

Spectra were obtained on a Perkin-Elmer 781 spectrometer. Liquid samples were examined as thin films and solid materials analysed as nujol mulls, both on sodium chloride plates. Solution spectra were determined in a suitable solvent using matched sodium chloride cells of pathlength 0.1 mm. All spectra were calibrated using the polystyrene reference absorption at 1603 cm^{-1}.

iii. Raman spectroscopy

Raman spectra were run and assigned by Dr J.R. Walton and Miss H.J. Bowley, Project 203, Spectroscopy Branch, BP Research Centre, Sunbury, using an Annaspec 33 Laser Raman Spectrometer equipped with a Spectra Physics Model 171 Ar ion laser (457.9 nm excitation).

iv. Mass spectroscopy (MS)

α. Electron impact (EI) mass spectroscopy

All spectra refer to those obtained using this technique, unless otherwise indicated. EI spectra were run on an Associated Electrical Industries MS-902 instrument operated by Mr D.J.A. Thomas, Ms E. Stevenson or Mr A. Taylor. Accurate mass measurements were also determined on this machine.

β. Chemical ionisation (CI) mass spectroscopy

Several CI mass spectra were obtained using a Kratos MS 80 instrument operated by Mr G. Gough, Spectroscopy Branch, BP Research Centre.

γ. Fast atom bombardment (FAB) mass spectroscopy

FAB mass spectra were obtained courtesy of Dr K.J. Bare, BP Research Centre, operating a Kratos MS 50 spectrometer.

δ. Gas chromatography-mass spectroscopy (GC-MS)

These spectra were furnished by Ms E. Stevenson, University of Edinburgh, operating a Pye series 104 gas chromatograph coupled to a V.G. Micromass 12 spectrometer; Mr G. Gough, BP Research Centre, also provided a number of spectra by use of a Kratos MS 80 instrument.

v. Ultraviolet (UV) spectroscopy

UV spectra were run on a Unicam SP 800A spectrophotometer using matched 1 cm quartz cells.

3. Specific reaction techniques and instrumentation

a. Photochemical reactions

Photochemical reactions were conducted using 100W or 400W medium pressure mercury lamps and appropriate power supplies, available from Applied Photophysics Limited. The lamps were placed inside water-cooled pyrex or quartz immersion wells which were then inserted into a vessel containing the reaction solution to be irradiated. In the case of small scale reactions, the reactants were placed in a suitably sized quartz or pyrex test-tube which was then fastened directly to the relevant immersion well. Alternatively, the reactant solution could be placed in a quartz or pyrex NMR tube (5 mm diameter) and irradiated using an Applied Photophysics semi-micro photochemical reactor incorporating a 15W lamp with main emission band at 254 nm.

b. Vacuum pyrolyses

i. Flash vacuum pyrolysis (FVP)

The FVP apparatus used, illustrated in Figure 44, was based on the design of W.D. Crow, Australian National University, as described recently by Brown[222]. In terms of procedure, the material (generally 2-200 mg) to be pyrolysed was placed in the inlet tube and this attached (*via* a ground glass quickfit joint) to a silica pyrolysis tube (30 x 2.5 cm). The system was then evacuated to give a pressure of 10^{-3} mm Hg using an Edwards ED100 high capacity rotary oil pump, with the pressure being measured by a Pirani gauge situated between the product trap and the pump. On the requisite vacuum of *ca* 10^{-3} mm being attained, the sample was heated by means of a Buchi Kugelrohr oven (up to a maximum of 250°C) to enable complete volatisation of the sample over a period, dependent on sample size, of 20 min - 2h. The rate of volatilisation was adjusted (*via* the inlet temperature) to ensure that no appreciable rise in system pressure during volatilisation occurred. On volatilisation, the gaseous sample was immediately drawn through the pyrolysis tube, which was thermostatically maintained at the chosen pyrolysis temperature (normally within the range 300-1000°C) by means of a Stanton Redcroft LM 8100 tube furnace incorporating a centrally loated Pt/Pt-13% Rh thermocouple. Under these conditions the contact time in the hot zone is estimated to be of the order of milliseconds. The pyrolysate was then collected in the product trap which was cooled by immersion in a liquid nitrogen bath.

Following complete volatilisation of the sample, the pump was isolated from the rest of the vacuum system to which was then admitted an atmosphere of dry nitrogen *via* an attached balloon. After removal

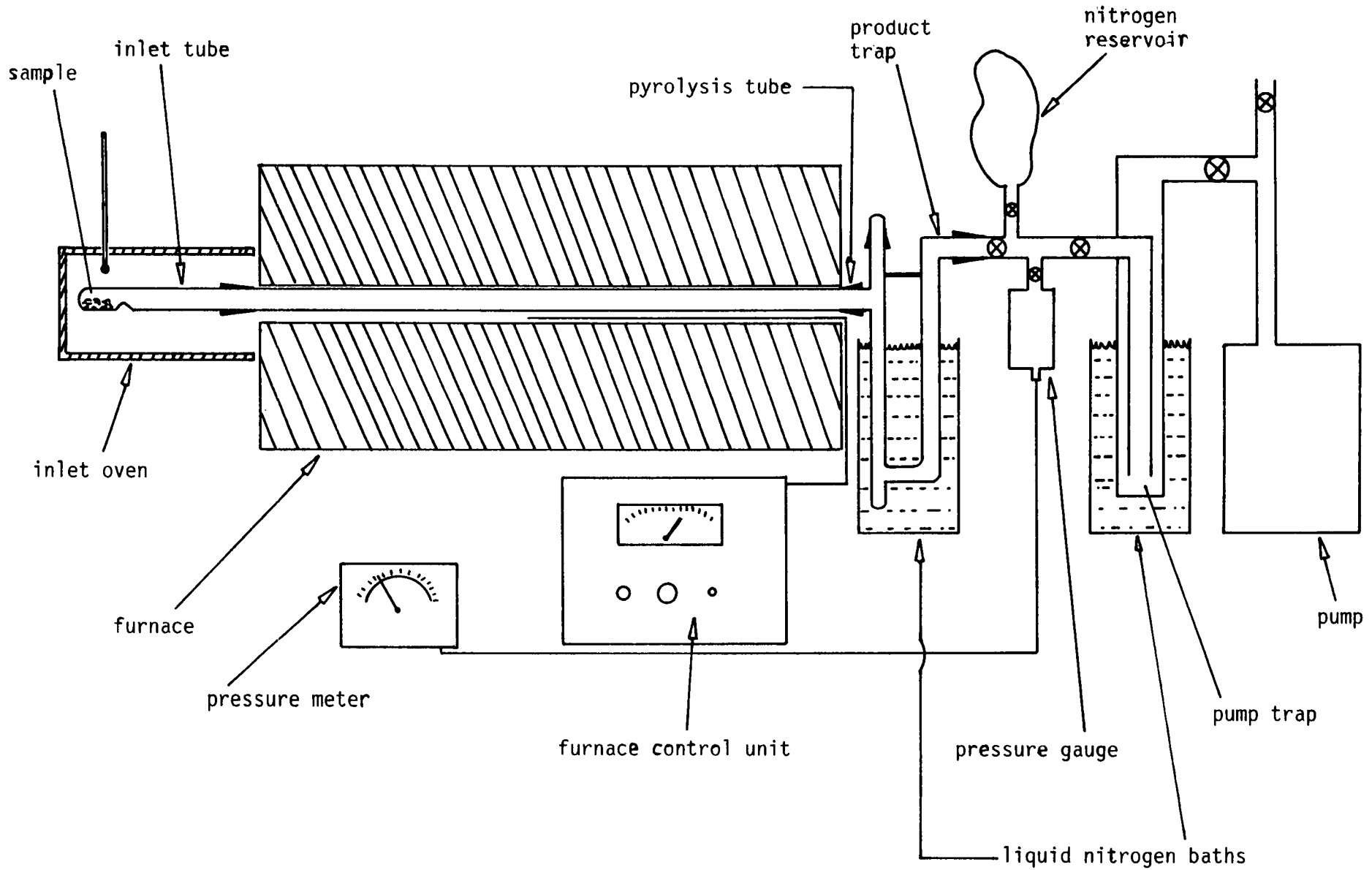


Figure 44 : Representation of FVP apparatus

of the liquid nitrogen bath, a suitable solvent was added to the products whilst these were still very cold enabling dissolution of volatile and/or thermally unstable compounds in a form suitable for analysis to be undertaken. Often deuterated solvents were used to dissolve the products for analysis by ^{1}H NMR spectroscopy; addition of measured quantities (2-30 mg) of non-deuterated solvents (e.g. methylene chloride) which display signals in an unoccupied region of the product spectrum enabled calculation of crude yields to be made following comparison of integration heights.

The conditions employed during FVP of samples are described later in this section using the following format: [inlet oven temperature, furnace (pyrolysis) temperature, average pressure during FVP)].

ii. Vertical vacuum pyrolysis (VVP)

This technique may be used to effect the in vacuo pyrolysis of materials which, due to their involatility, cannot be submitted to FVP. As displayed in Figure 45, the VVP apparatus incorporates the same basic instrumentation as that used in FVP except that the pyrolysis tube and furnace are mounted vertically and the FVP inlet is replaced by a dropping head incorporating a rotating spatular sample holder. Pyrolysis was achieved by slowly rotating the sample holder so that the neat sample was allowed to fall, in several portions over a period of a few minutes into the pyrolysis tube where it contacted a 2 cm quartz wool plug situated at the mid-point of the hot tube. The pyrolysate was collected in the product trap (immersed in a liquid nitrogen bath) and the products were then obtained by an identical procedure to that described for the FVP technique. As the contact time of material in the hot zone is very much longer than that for FVP, this type of pyrolysis does not merit the 'flash vacuum' label, the term 'vacuum pyrolysis' being more accurate.

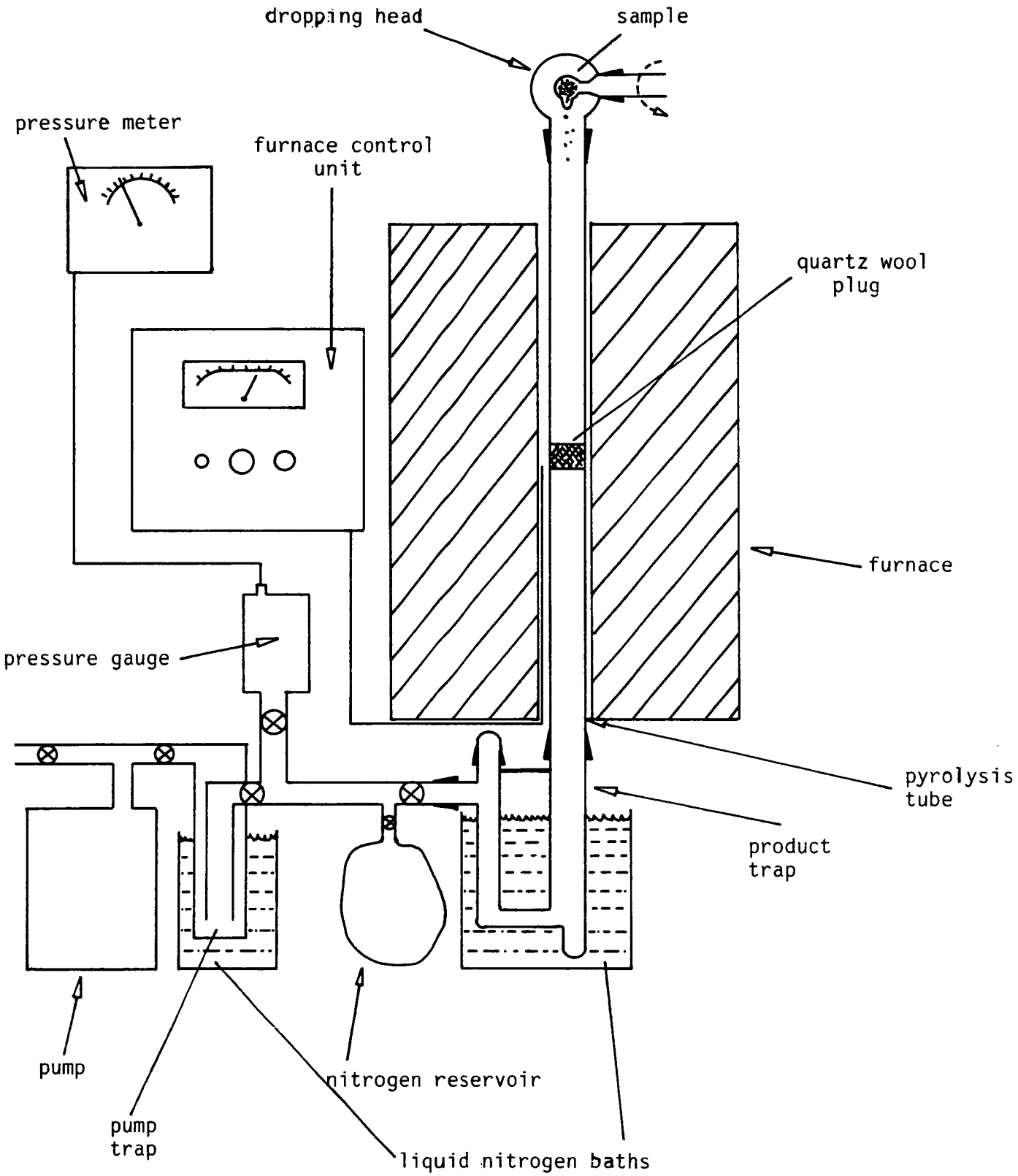


Figure 45 : Representation of VVP apparatus

A. Preparation of (cis-1-transoid-1,2-cis-2)-4-Thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208)

1. From cis-1-transoid-1,2-cis-2-bicyclo[2.2.0]hex-5-ene-exo-cis-2,3-dicarboxylic anhydride (214)

a. Preparation of cis-1-transoid-1,2-cis-2-bicyclo[2.2.0]-hex-5-ene-exo-cis-2,3-dicarboxylic anhydride (214)

i. cis-1,2-Dihydrophthalic anhydride (216)

The procedure used was based on that of McDonald and Reineke[100]. A suspension of an equimolar mixture of cis- and trans-1,2-dihydrophthalic acid (217) (x BASF; 25.00g, 0.149 mol) in acetic anhydride (110 ml) was stirred at room temperature for 3h, and then at 40°C for 10 min. The resultant solution was evaporated to dryness in vacuo and the dark yellow crystalline residue sublimed at 100°C, 0.1 mm Hg. Recrystallisation of the sublimed material from dry benzene gave cis-1,2-dihydrophthalic anhydride (216) (12.37g, 55%) as colourless crystals, m.p. 104-107°C (lit.[100] m.p. 108-109.5°C).

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.79 (dd, J = 1.7 Hz, 0.9 Hz; 2H), 5.72-5.91 (cm; 2H), 6.00-6.24 (cm; 2H); UV (ether) $\lambda_{max.}$ [nm]: 256, 265 (lit.[100] $\lambda_{max.}$ [nm]: 256, 264). The ^{1}H NMR spectrum indicated the presence of phthalic anhydride (ca 10%), though the product was used in the next stage without further purification.

ii. cis-1-transoid-1,2-cis-2-bicyclo[2.2.0]hex-5-ene-exo-cis-2,3-dicarboxylic anhydride (214)

This was obtained following a slight modification of the procedure described by McDonald and Reineke[100]. A stirred solution of cis-1,2-dihydrophthalic anhydride (216) (1.708g, 12.2 mmol) in dry ether (600 ml) was photolysed under a nitrogen atmosphere using a

400W lamp contained in a quartz immersion well. The course of the reaction was followed by monitoring the decrease in UV absorption of the diene ($\lambda_{max.}$ 256, 265 nm) which was found to have reached a constant minimum after irradiation for 5h. After filtering off a small quantity of colourless polymeric solid, the ethereal filtrate was evaporated in vacuo to yield a viscous yellow oil which solidified. Sublimation of this at 100°C, 0.2 mm Hg gave cis-1-transoid-1,2-cis-2-bicyclo[2.2.0]hex-5-ene-exo-cis-2,3-dicarboxylic anhydride (214) (0.239g, 14%) as colourless cubic crystals, m.p. 161-163°C (lit.[98] m.p. 162-163°C), on recrystallisation from dry methylene chloride/dry ether.

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.38 (t, J = 1.0 Hz; 2H), 3.63-3.69 (m; 2H), 6.45 (d, J = 3.0 Hz; 2H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 44.77, 46.98, 141.89, 171.39 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1841, 1766, 1282, 1236, 1200, 1169, 1073, 956, 937, 918, 886, 842, 758, 688, 659; MS [EI] m/e (%): 150 (3; M^+), 105 (2), 91 (2), 79 (36), 78 (100), 77 (44), 63 (28), 52 (40).

b. Preparation of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo [5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208)

i. exo-cis-2,3-Bis(hydroxymethyl)-cis-bicyclo[2.2.0]hex-5-ene (218)

A solution of cis-1-transoid-1,2-cis-2-bicyclo [2.2.0] hex-5-ene-exo-cis-2,3-dicarboxylic anhydride (214) (0.666g, 4.76 mmol) in dry tetrahydrofuran (15 ml) was added dropwise, over 25 min, to a suspension of lithium aluminium hydride (0.248g, 6.53 mmol) in dry tetrahydrofuran (9 ml) stirred under a nitrogen atmosphere. On completion of addition, the resultant dark green mixture was stirred under nitrogen and heated under reflux for 2h. On cooling, the excess of lithium aluminium hydride was destroyed by sequential addition of water (0.5 ml) in tetrahydrofuran (3.5 ml), 15% sodium hydroxide

solution (0.5 ml), and finally water (3 ml). The now colourless inorganic salts were filtered off, washed thoroughly with tetrahydrofuran, and the combined filtrates evaporated in vacuo. Redissolution of the residue in methylene chloride (50 ml), followed by drying of the solution with anhydrous magnesium sulphate, gave on filtration and evaporation a cloudy, yellow oil.

TLC (silica; ether) of this indicated the presence of a major component R_f 0.18, together with minor components R_f 0.18 and 0.09. Following MPLC (silica; gradient elution : petroleum-ether (b.p. 40-60°C) → ether) the major component, exo-cis-2,3-bis(hydroxymethyl)-cis-bicyclo[2.2.0]hex-5-ene (218) (0.297g, 48%), was obtained as a colourless oil.

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.25-2.51 (m; 2H), 2.78 (quintet, J = 1.2 Hz; 2H), 3.04 (bd s; 2H), 3.46-3.92 (m; 4H), 6.31 (t,J=1.2 Hz; 2H) [compares well with lit.[101] ^{1}H NMR]; ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.19 (CH), 42.80 (CH), 61.82 (CH_2), 141.04 (CH); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 3305, 1546, 1452, 1293, 1111, 1032, 908, 896, 746; MS [EI] m/e (%): 140 (10; M^+), 122 (13), 107 (13), 92 (57), 91 (74), 79 (100), 77 (38), 73 (41).

ii. exo-cis-Bis(p-toluenesulphonyloxymethyl)-cis-bicyclo-[2.2.0]hex-5-ene (219)

A variation of the conditions employed by Farr and Bauld[101] was employed. A solution of exo-cis-2,3-bis(hydroxymethyl)-cis-bicyclo[2.2.0]hex-5-ene (218) (0.256g, 1.83 mmol) in pyridine (5 ml) was added dropwise, over a 40 min period, to a stirred suspension of p-toluene sulphonyl chloride (2.231g, 11.7 mmol) in pyridine (5 ml) at 0°C. After stirring at 0°C for 3h, the mixture was added to iced water (100 ml) with immediate precipitation of a colourless solid.

Dilute hydrochloric acid solution was added until the mixture was slightly acidic. The solid present was filtered off, washed well with water, and dried *in vacuo* (room temperature, 0.05 mm Hg) to give *exo-cis-bis(p-toluenesulphonyloxymethyl)-cis-bicyclo[2.2.0]hex-5-ene* (219) (0.484g, 59%) as fine white needles, m.p. 144-145°C (lit.[101] m.p. 146-147°C) on recrystallisation from methanol.

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.31-2.54 (bd m; 8H), 2.96 (t, $J_{1,5}(J_{4,6}) = J_{1,6}(J_{4,5}) = 1.2$ Hz; H_1, H_4), 4.02-4.16 (m; 4H), 6.24 (t, $J_{1,5}(J_{4,6}) = J_{1,6}(J_{4,5}) = 1.2$ Hz; H_5, H_6), 7.35 and 7.76 (A_2B_2 pattern, J = 8.4 Hz; 8H) [compares well with lit.[101] ^{1}H NMR]; *^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]*: 21.38, 35.42, 43.45, 69.30, 127.62 (2xCH), 129.76 (2xCH), 132.72 (Q), 141.26, 144.76 (Q); *IR (nujol) $\nu_{max.}$ [cm^{-1}]*: 1597, 1347, 1190, 1171, 1098, 943, 832, 819, 738, 665; *MS [EI] m/e (%)*: 448 (0.1; M^+), 327 (0.5), 293 (0.3), 276 (1), 227 (3), 181 (6), 172 (5), 155 (61), 122 (8), 121 (8), 104 (100), 91 (55), 65 (35).

iii. (*cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]-non-8-ene (220)*

To a solution of *exo-cis*-bis(*p*-toluenesulphonyloxymethyl)-*cis*-bicyclo[2.2.0]hex-5-ene (219) (0.240g, 0.536 mmol) in ethanol (7 ml) was added a solution of sodium sulphide nonahydrate (0.406g, 1.69 mmol) in water (7 ml). The resultant mixture was stirred and heated under reflux for 3h, by which time monitoring by TLC (silica; ether) indicated the absence of starting ditosylate, R_f 0.60. Extraction of the cooled product solution with methylene chloride (5x10 ml) followed by evaporation *in vacuo* gave a semi-crystalline residue. To this was added methylene chloride (50 ml) and the resultant organic solution

decanted from insoluble inorganic materials, dried over anhydrous magnesium sulphate, filtered and the filtrate evaporated *in vacuo* to give (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.0^{2,6}]non-8-ene (220) (55 mg, 74%) as a foul-smelling light yellow oil, used in the next reaction stage without further purification.

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.55-3.02 (m; 8H), 6.22 (d, J = 0.9 Hz; 2H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 37.99 (CH_2), 45.49 (CH), 48.05 (CH), 140.04 (CH); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 3028, 2930, 1546, 1432, 1371, 1298, 1217, 1102, 909, 850, 736, 707; MS [EI] m/e (%): 138 (10; M^+), 105 (3), 92 (15), 91 (33), 85 (5), 78 (5), 77 (7), 65 (7), 60 (100), 59 (18), 52 (6), 51 (6), 45 (19), 32 (15).

iv. (*cis*-1-*transoid*-1,2-*cis*-2)-4-Thiatricyclo[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208)

To a stirred solution of (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.0^{2,6}]non-8-ene (220) (33 mg, 0.239 mmol) in dry ether (2 ml) at 0°C was added dropwise, over a 25 min period, a solution of *m*-chloroperoxybenzoic acid (103 mg '85%' = 88 mg 100%, 0.508 mmol) in dry ether (6 ml) with precipitation of a little cream-coloured solid. The mixture was stirred at 0°C for 30 min, and then at room temperature for 70h at which time TLC (silica; ether) indicated the absence of starting sulphide (R_f 0.80) and the presence of a single product spot (R_f 0.46). Methylene chloride (15 ml) was added to the mixture and the resultant solution was washed with 80% saturated sodium carbonate solution (3x10 ml), dried over anhydrous magnesium sulphate and the dried filtrate evaporated *in vacuo* to generate a light yellow solid (31 mg). Purification by preparative TLC (silica; ether) gave as a colourless crystalline solid, (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.0^{2,6}] non-8-ene 4,4-dioxide (208) (18 mg, 44%),

obtained as colourless prisms suitable for X-ray diffraction study), m.p. 109-111.5°C on recrystallisation from methylene chloride/diisopropyl ether.

EA: $C_8H_{10}O_2S$ requires 56.4% C, 5.9% H; found 56.3% C, 5.7% H; ^1H NMR ($CDCl_3$; 360 MHz) δ [ppm]: 2.83-2.87 (sym m; H_2, H_6), 2.97-3.03 (sym m; H_{3b}, H_{5b}), 3.22-3.23 (sym m; H_1, H_7), 3.24-3.30 (sym m; H_{3a}, H_{5a}), 6.34 (dist. dd, $J_{1,8}(J_{7,9})$ = 1.4 Hz, $J_{1,9}(J_{7,8})$ = 1.2 Hz; H_8, H_9). Assignment of signals to protons were made on the basis of ^1H NOE difference spectra and following selective ^1H NMR decoupling studies which allowed determination of coupling constants: $J_{1,2}(J_{6,7})$ = $J_{1,6}(J_{2,7})$ = $J_{1,9}(J_{7,8})$ = 1.2 Hz, $J_{1,8}(J_{7,9})$ = 1.4 Hz, $J_{2,3a}(J_{5a,6})$ = 8.7 Hz, $J_{2,3b}$ ($J_{5b,6}$) = 2.6 Hz, $J_{2,5a}(J_{3a,6})$ = 1.2 Hz, $J_{3a,3b}(J_{5a,5b})$ = 13.9 Hz; ^{13}C NMR ($CDCl_3$; 25 MHz) and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 34.44 (CH), 47.85 (CH), 53.96 (CH_2), 141.19 (CH); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1297 (SO_2), 1254, 1228, 1166, 1142 (SO_2), 1098, 917, 890, 852, 753, 703; MS [EI] m/e (%): 170 (10; M^+), 105 (50), 104 (31), 92 (22), 91 (100), 79 (41), 78 (95), 77 (33), 64 (26).

2. From cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212)

a. Preparation of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212)

i. From cis-1,2-dihydrophthalic anhydride (216)

α. cis-5,6-Bis(hydroxymethyl)cyclohexa-1,3-diene (221)

A solution of cis-1,2-dihydrophthalic anhydride (216) (10.00g, 66.7 mmol) in dry tetrahydrofuran (90 ml) was added dropwise, over a 10 min period, to a stirred suspension of lithium aluminium hydride (5.40g, 0.142 mol) in dry tetrahydrofuran (200 ml) under a nitrogen atmosphere. The resultant warm, yellow mixture was heated

under reflux for 3h, still under a nitrogen atmosphere, and on cooling the excess of lithium aluminium hydride was destroyed by sequential addition of water (5 ml) in tetrahydrofuran (30 ml) and then 15% sodium hydroxide solution (5 ml). After filtration of the inorganic salts, these were boiled in acetone for 2h and the acetone solution decanted from the residual inorganic salts and added to the initial tetrahydrofuran filtrate. On evaporation in vacuo, the residue obtained was redissolved in methylene chloride (100 ml), dried over anhydrous magnesium sulphate and the dried filtrate evaporated to leave an orange oil. Distillation under reduced pressure gave cis-5,6-bis-(hydroxymethyl)cyclohexa-1,3-diene (221) (6.80g, 73%) as a viscous light yellow oil, b.p. 126-128°C at 0.9 mm Hg, n_D^{19} 1.5158.

EA: $C_8H_{12}O_2$ requires 68.6% C, 8.6% H; found 68.6% C, 8.6% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm] : 2.42-2.71 (m; 2H), 3.45-3.82 (m; 4H), 4.19 (bd s; 2H), 5.54-5.66 (m; 2H), 5.85-5.97 (m; 2H); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 3320, 3034, 2924, 2880, 1694, 1433, 1376, 1204, 1098, 1032, 944, 754, 690; MS [EI] m/e (%): 141 (3; $(M+1)^+$), 140 (7), 120 (10), 119 (9), 110 (16), 92 (45), 91 (41), 79 (100), 59 (22).

β. cis-5,6-Bis(p-toluenesulphonyloxymethyl)cyclohexa-1,3-diene (222)

A solution of cis-5,6-bis(hydroxymethyl)cyclohexa-1,3-diene (221) (5.04g, 36.0 mmol) in pyridine (50 ml) was added dropwise, over a 50 min period, to a stirred solution of p-toluene sulphonyl chloride (22.92g, 0.120 mol) in pyridine (50 ml) at 0°C. After stirring at 0°C for a further 3h, the orange solution was poured into iced water (200 ml). Dilute sulphuric acid was added until the mixture became slightly acidic, after which it was extracted with methylene chloride (3x100 ml). The extracts were combined, dried over anhydrous magnesium sulphate, and the dried filtrate evaporated to give, as a light orange

oil which solidified on standing, cis-5,6-bis(p-toluenesulphonyloxymethyl)-cyclohexa-1,3-diene (222) (11.92g, 74%), m.p. 68.5-70°C on recrystallisation from isopropanol.

EA: $C_{22}H_{24}O_6S_2$ requires 58.9% C, 5.4% H; found 58.7% C, 5.5% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.44 (s; 6H), 2.75-2.78 (sym m; 2H), 3.90-4.02 (m; 4H), 5.52-5.59 (m; 2H), 5.89-5.94 (m; 2H), 7.34 and 7.75 (A_2B_2 pattern, J=8.1 Hz; 8H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 21.33, 34.85, 68.00, 124.65, 125.62, 127.57 (2xCH), 129.68 (2xCH), 132.46 (Q), 144.73 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1597, 1363, 1175, 1094, 945, 889, 854, 828, 817, 803, 789, 698, 667; MS [EI] m/e (%): M^+ not apparent, 303 (16), 281 (5), 207 (6), 172 (99), 155 (15), 108 (46), 107 (77), 91 (100).

On exposure to air the material decomposed, over a period of several weeks, to give a black tar.

γ. Preparation of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212)

(1) Using aqueous ethanol as solvent

To a solution of cis-5,6-bis(p-toluenesulphonyloxymethyl)-cyclohexa-1,3-diene (222) (2.00g, 4.46 mmol) in ethanol (30 ml) was added a solution of sodium sulphide nonahydrate (3.21g, 13.4 mmol) in water (30 ml) and the resultant mixture heated under reflux with stirring for 65h. On cooling, the ethanol was removed by evaporation in vacuo and the residual aqueous phase extracted with methylene chloride (3x50 ml). The combined extracts were dried over anhydrous magnesium sulphate and the dried filtrate evaporated in vacuo to give a brown, waxy solid (0.51g). Kugelrohr distillation at 100-110°C, 0.5 mm Hg resulted in isolation of a small quantity (19 mg) of a yellow oil:

^{1}H NMR analysis of this indicated the presence of only aromatic products. No further products were obtained on distillation at higher temperatures. In view of the absence of olefinic sulphide products the next stage (oxidation to sulphone products) was not pursued.

(2) Using anhydrous HMPA as solvent

The method described by Paquette et al[105] was utilised. A mixture of sodium sulphide nonahydrate (29.50g, 0.123 mol) in hexamethylphosphoramide (HMPA) (100 ml) was dehydrated by distilling off a fraction (20 ml) up to a stillhead temperature of 70°C at 0.6 mm Hg. On cooling, the deep blue anhydrous solution of sodium sulphide in HMPA was decanted from some residual solid material present, then added to cis-5,6-bis(p-toluenesulphonyloxymethyl)cyclohexa-1,3-diene (222) (5.00g, 11.2 mmol). The resultant brown solution was stirred at room temperature for 70h by which time TLC (alumina; ether) monitoring indicated the absence of ditosylate (R_f 0.76).

Water (50 ml) and ether (200 ml) were added, and the organic layer separated. The aqueous layer was extracted with ether (3x125 ml), the four organic fractions combined, washed with water (3x100 ml), dried over anhydrous magnesium sulphate and the dried filtrate evaporated in vacuo to give a viscous orange oil. Following Kugelrohr distillation (60-70°C, 0.2 mm Hg) then column chromatography (6% deactivated alumina; ether), a light yellow oil (0.52g) was obtained. ^{1}H NMR analysis of this indicated the presence of mainly aromatic sulphide products, including benzyl methyl sulphide identified by comparison with a published[223] spectrum, although some olefinic signals were also observed.

The sulphide products (0.52g, est. 3.77 mmol) were dissolved in dry ether (10 ml) and the solution stirred at 0°C during the dropwise addition, over a 45 min period, of a solution of m-chloroperoxybenzoic acid (1.62g '85%' = 1.38g 100%, 7.98 mmol) in dry ether (30 ml). After stirring at room temperature for 43h, the product mixture was washed with saturated sodium carbonate solution (100 ml) then dried over anhydrous magnesium sulphate. Evaporation of the dried filtrate gave a colourless crystalline residue (0.282g) which was found by TLC (silica; ether) analysis to contain three main product spots. Preparative TLC (silica; ether) of a portion (69.8 mg) of the crude sulphone product mixture gave three separated bands:

(a) R_f 0.48, a colourless crystalline solid identified as benzyl methyl sulphone (226) (13.1 mg, 3% from (222)), m.p. 125-128°C (lit.[224] m.p. 125-127°C) on recrystallisation from methylene chloride/diisopropyl ether. ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.74 (s; 3H), 4.24 (s; 2H), 7.41 (s; 5H); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1458, 1321, 1303 (SO_2), 1251, 1156, 1117 (SO_2), 967, 885, 787.

(b) R_f 0.75, a colourless crystalline material identified as 3,4-benzo-1-thiacyclopent-3-ene 1,1-dioxide (110) (10.2 mg, 2% from (222)), obtained as colourless rhombs, m.p. 149-150°C (lit.[202] m.p. 150-152°C) on recrystallisation from chloroform/diisopropyl ether. ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 4.35 (s; 4H), 7.32 (s; 4H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 56.86, 125.92, 128.67, 131.24 (Q) (similar to lit.[225] ^{13}C NMR); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1313, 1302 (SO_2), 1237, 1206, 1132, 1103 (SO_2), 903, 802, 771, 756; MS [EI] m/e (%): 168 (48; M^+), 104 (100), 103 (71), 78 (77), 77 (39), 63 (21), 52 (27), 51 (62).

(c) R_f 0.58, a light yellow oil (13.5 mg) containing cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (est. 1% from (222)), identified by comparison with an authentic sample prepared as described later, together with unidentified unsaturated (olefinic) products.

ii. From cis-8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (65)

α. cis-8-Thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (65)

The procedure of Aitken[33] was followed. To a stirred solution of cis-8-thiabicyclo[4.3.0]non-3-ene[140] (5.73g, 40.9 mmol) in dry ether (60 ml) at 0°C was added, dropwise over a 50 min period, a solution of m-chloroperoxybenzoic acid (17.44g '85%' = 14.82g 100%, 85.9 mmol) in dry ether (220 ml). After stirring at 0°C for 30 mins, and then at room temperature for 65h, the product mixture was washed with sodium carbonate solution, dried over anhydrous magnesium sulphate and the dried filtrate evaporated *in vacuo*. Recrystallisation of the residue from ether gave cis-8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (65) (4.70g, 67%) as colourless crystals, m.p. 69-72°C (lit.[33] m.p. 73-74°C).

β. trans-3,4-Dibromo-cis-8-thiabicyclo[4.3.0]nonane 8,8-dioxide (229)

A solution of cis-8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (65) (2.90g, 16.9 mmol) in methylene chloride (15 ml) was stirred at -78°C during the dropwise addition, over 20 min, of a solution of bromine (3.29g; 20.6 mmol) in methylene chloride (3 ml). After stirring at -78°C for a further 30 mins, the mixture was allowed to warm to room temperature and reduced *in vacuo* to reveal a yellow powder. On recrystallisation from isopropanol, colourless needles

of trans-3,4-dibromo-cis-8-thiabicyclo[4.3.0]nonane 8,8-dioxide (229) (5.26g, 94%), m.p. 190.5-192°C, were obtained.

EA: $C_8H_{12}Br_2O_2S$ requires 28.9% C, 3.6% H; found 29.1% C, 3.7% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.90-3.28 (m; 9H), 3.48-3.74 (m; 1H), 4.18-4.57 (m; 2H); ^{13}C NMR (CD_3SOCD_3; 25 MHz) δ [ppm]: 36.11, 36.51, 36.93, 37.31, 51.46, 53.38, 55.76, 57.92; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1293 (SO_2), 1249, 1221, 1200, 1122 (SO_2), 1078, 1004, 966, 877, 771, 733, 679; MS [EI] m/e (%): M^+ not apparent, 270 (7), 268 (14), 266 (7), 253 (43), 251 (40), 189 (32), 187 (40), 171 (42), 107 (90), 105 (100), 91 (58).

γ. cis-8-Thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212)

The general procedure of Warner and Lu[106] was used. A suspension of trans-3,4-dibromo-cis-8-thiabicyclo[4.3.0]nonane 8,8-dioxide (229) (11.48g, 34.6 mmol) in dry tetrahydrofuran (35 ml) was stirred at room temperature under nitrogen during the dropwise addition, over 40 min, of a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (16.97g, 0.112 mol) in dry tetrahydrofuran (45 ml). After stirring at 45°C for 48h, the resultant yellow mixture was cooled and water (40 ml) added. Extraction of the aqueous solution with methylene chloride (4x80 ml), followed by sequential washing of the combined organic extracts with 0.1M hydrochloric acid solution (250 ml), saturated sodium chloride solution (60 ml), and water (60 ml) gave, after drying over anhydrous magnesium sulphate and evaporation in vacuo of the dried filtrate, a viscous brown oil (4.57g).

TLC (silica; ether) analysis indicated the presence of two, UV-active, components R_f 0.39 and 0.29. MPLC (silica; 50:50 petroleum-ether (b.p. 40-60°C): ether → ether; 140 → 400 kN/m^2) of a portion (2.40g) gave the two separated components:

(a) R_f 0.39, a colourless oil which crystallised on cooling to -20°C. Recrystallisation from diisopropyl ether gave colourless flakes of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (1.42g, 46%), m.p. 35-36.5°C.

EA: $C_8H_{10}O_2S$ requires 56.4% C, 5.9% H; found 56.3% C, 5.9% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.92-3.28 (bd s; 6H), 5.46-5.69 (m; 2H), 5.79-6.03 (m; 2H); ^{13}C NMR ($CDCl_3$; 90.3 MHz) δ [ppm]: 34.38, 54.90, 124.79, 126.02; IR (neat film-melt) $\nu_{max.}$ [cm^{-1}]: 3400, 2948, 1407, 1371, 1303 (SO_2), 1217, 1123 (SO_2), 978, 867, 786, 757, 698, 645; MS [EI] m/e (%): 170 (32; M^+), 105 (38), 104 (25), 92 (26), 91 (100), 79 (16), 78 (47), 77 (14), 65 (12); UV (ether) $\lambda_{max.}$ [nm] ($\epsilon_{max.}$): 264 (3640), 274 (3250).

(b) R_f 0.29, a crystalline solid identified as 8-thiabicyclo [4.3.0]nona-1,3-diene 8,8-dioxide (230) (0.32g, 10%), obtained as colourless needles, m.p. 112-113.5°C, on recrystallisation from diisopropyl ether.

EA: $C_8H_{10}O_2S$ requires 56.4% C, 5.9% H; found 56.3% C, 5.7% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 1.39-1.60 (m; 1H), 2.03-2.15 (m; 1H), 2.31-2.38 (m; 2H), 2.84-2.94 (m; 1H), 3.06-3.24 (m; 1H), 3.43-3.52 (m; 1H), 6.22 (d, J = 2.0 Hz; 1H), 6.31-6.33 (m; 2H); ^{13}C Off-resonance decoupled NMR ($CDCl_3$; 25 MHz) δ [ppm]: 25.47 (t), 27.77 (t), 36.38 (d), 55.88 (t), 121.47 (d), 122.54 (d), 140.12 (d), 148.59 (s); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1628, 1578, 1427, 1276 (SO_2), 1239, 1226, 1188, 1150, 1127, 1099 (SO_2), 853, 810; MS [EI] m/e (%): 170 (26; M^+), 153 (17), 141 (40), 122 (26), 107 (72), 91 (100), 79 (90), 77 (61).

Stirred solutions of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (47.6 mg, 0.28 mmol) and 1,8-diazobicyclo[5.4.0]-

undec-7-ene (DBU) (49.2 mg, 0.32 mmol) in dry tetrahydrofuran (0.5 ml), and of 8-thiabicyclo[4.3.0]nona-1,3-diene 8,8-dioxide (230) (45 mg, 0.26 mmol) and DBU (50 mg, 0.33 mmol) in dry tetrahydrofuran (2 ml) were heated at 45°C for 48h. Analyses of both solutions after this time by TLC (silica; ether) and by ^{1}H NMR spectroscopy (of the evaporated product solutions) indicated that the starting diene was recovered quantitatively in each case; no isomerisation of one diene to the alternative isomer or to any other product was apparent.

δ. FVP of trans-3,4-dibromo-cis-8-thiabicyclo[4.3.0]nonane 8,8-dioxide (229)

(1) Small scale

FVP (170°C, 650°C, 5 x 10^{-3} mm Hg] of the title compound (229) (38.3 mg, 0.115 mmol) gave a pyrolysate consisting of a mixture of a colourless oil and solid. GLC analysis (10% PEGA; 90°C) indicated the presence of o-xylene (24% from (229)), ethyl benzene (5%) and styrene (1%); TLC (silica; ether) indicated the presence of a single non-volatile product (R_f 0.39) and following preparative TLC (silica; ether) of the pyrolysate, a colourless oil, identified as cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (8.2 mg, 42%) by comparison of ^{1}H NMR spectra with an authentic sample, was isolated.

(2) Large scale

FVP [165°C, 650°C, 8x10^{-3} mm Hg] of the title compound (229) (2.384g, 7.18 mmol) over a 3h period resulted in isolation of a dark yellow/brown liquid (1.964g). ^{1}H NMR and TLC (silica; ether) analyses indicated this to be a highly complex mixture of products in which little or no diene (212) was present.

b. Photolysis of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) and related systems

i. Photolysis of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212)

α. A solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (86.4 mg, 0.51 mmol) in ether (75 ml) was deoxygenated by nitrogen ebullition for 30 min. It was then irradiated using a 400W lamp through a quartz immersion well fitted with a Vycor filter, with nitrogen ebullition. The decrease in diene absorption of (212) ($\lambda_{max.}$ 264, 274 nm) in the UV spectrum was monitored regularly during irradiation, these being found to have decreased to a minimum after photolysis for 9.5h. After removal of a small quantity (6 mg) of an unidentified polymeric solid, the filtrate was evaporated in vacuo to give a viscous brown oil (138 mg). Analysis of the ^{1}H NMR spectrum confirmed the absence of starting diene (212); no olefinic resonances were present and the only product identified - by comparison with an authentic sample - was 3,4-benzo-1-thiacyclopent-3-ene 1,1-dioxide (110) (est. 5 mg, 6%) [yield calculated by comparison of ^{1}H NMR integral heights of this product and added methylene chloride (12.0 mg)].

β. A solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (170 mg, 1.00 mmol) in ether (130 ml) was maintained at -78°C and, whilst undergoing nitrogen ebullition, was irradiated for 8h with a 100W lamp located in a quartz immersion well. Removal of solvent by evaporation in vacuo gave a light yellow oil (241 mg). TLC (silica; ether) indicated the presence of a single spot coincidental with starting diene (212); preparative TLC (silica; ether) gave purely recovered (212) (109 mg, 64%).

γ. A solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (63 mg, 0.37 mmol) in acetonitrile (75 ml) was irradiated through quartz using a 400W lamp, whilst undergoing constant nitrogen ebullition. The decrease in diene (212) absorption in the UV region was monitored at regular intervals and was found to have reached a constant minimum after irradiation for 6.5h. After removal of a colourless polymeric solid by filtration, and following evaporation of solvent, a colourless liquid (3 mg) was obtained which was found to contain no starting diene (212) and only 3,4-benzo-1-thiacyclopent-3-ene 1,1-dioxide (110) (est. 0.6 mg, 1%) as the sole identified product (following ^{1}H NMR analysis).

δ. A solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (65 mg) and benzophenone (81 mg) in acetone (50 ml) was irradiated (100W lamp) through quartz for 9h. Evaporation of the resultant solution gave a colourless oil which on ^{1}H NMR analysis was found to contain 3,4-benzo-1-thiacyclopent-3-ene 1,1-dioxide (110) (est. 2 mg, 3%) as the sole identified sulphone-containing product.

ε. A solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (55 mg, 0.32 mmol) in ether (0.5 ml), contained in a quartz NMR tube, was irradiated with a 15W (254 nm) lamp and the reaction monitored by TLC (silica; ether). This indicated a decrease in concentration of starting diene (212), R_f 0.39, with concomitant increase in formation of an UV active product, R_f 0.58, coincidental with the trans-fused diene (235), up to an irradiation period of two days. After this time, subsequent irradiation for four days resulted in no measureable change in ratio of the two component spots in TLC.

The mixture was evaporated to dryness, methylene chloride (10 ml) added and a little insoluble polymeric material removed by filtration. Evaporation of the filtrate gave a cream-coloured crystalline residue (48 mg) which, following ^{1}H NMR analysis (in deuteriochloroform containing added chloroform (21 mg)), was found to contain starting diene (212) (est. 21 mg, 38%), trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235) (est. 25.5 mg, 46%) and 3,4-benzo-1-thiacyclopent-3-ene 1,1-dioxide (110) (est. 1.5 mg, 3%). Preparative TLC (silica; ether) allowed separation of the two isomeric dienes, permitting verification of the presence of these by comparison of ^{1}H NMR spectra with authentic samples. An independent synthesis of (235) is described later (p.575).

ζ. Photolysis of a dilute solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (6 mg, 0.035 mmol) in ether (1.0 ml), contained in a quartz NMR tube, using a 15W (254 nm) lamp for 2h gave on evaporation a mixture of starting diene (212) (est. 3.0 mg, 50%), trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235) (est. 2.1 mg, 35%) and 3,4-benzo-1-thiacyclopent-3-ene 1,1-dioxide (110) (est. 0.3 mg, 5%), following ^{1}H NMR analysis.

Photolysis under identical conditions of a solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (6 mg, 0.035 mmol) in carbon tetrachloride (1.0 ml) for 2h resulted in formation of a mixture of starting diene (212) (est. 2.5 mg, 42%), trans-fused diene (235) (est. 0.2 mg, 3%) and benzosulpholene (110) (est. 0.3 mg, 5%), following ^{1}H NMR analysis of the evaporated photolysate.

ii. Photolysis of trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235)

A solution of trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235) (17 mg, 0.10 mmol) in ether (1.0 ml) was placed in a quartz NMR tube and irradiated with a 15W (254 nm) lamp. Monitoring of the progress of the reaction was achieved by TLC (silica; ether) which indicated only starting diene (235) to be present at all times, though the concentration of this decreased after irradiation for 6h due to increasing formation of a colourless polymeric precipitate. Irradiation was discontinued after a period of 21h: ^{1}H NMR analysis of the evaporated filtrate confirmed only the presence of starting diene (235).

Similar results were obtained on identical photolysis of a more dilute solution of (235) (4 mg) in ether (1.0 ml) for 5h.

iii. Photolysis of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208)

A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208) (19 mg, 0.11 mmol) in hexadeuterioacetone (0.7 ml) was placed in a quartz NMR tube and irradiated using a 100W lamp. The course of the photolysis was monitored by ^{1}H NMR spectroscopy and TLC (silica; ether) which both indicated that starting olefin (208) steadily decreased in concentration, being completely consumed after irradiation for 8h. No olefinic resonances other than those due to olefin (208) were observed at any time in the ^{1}H NMR spectra; TLC similarly did not display any product spots. Filtration of the product mixture gave a colourless solid (2 mg) and ^{1}H NMR analysis of this, and of the acetone filtrate (which contained purely saturated resonances), was indicative of polymeric materials.

3. From cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63)

a. Preparation of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63)

i. cis-3-Thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarboxylic anhydride 3,3-dioxide (45)

A slight modification of the procedure of Shaikhrazieva et al[27] was adopted. A solution of butadiene sulphone (30.00g, 0.254 mol) and maleic anhydride (30.00g, 0.306 mol) in acetone (400 ml), to which was added a few seed crystals of the desired product (45), was irradiated using a 400W lamp, through a pyrex immersion well, for five days. The colourless crystals were filtered off, washed with acetone and dried to give cis-3-thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarboxylic anhydride 3,3-dioxide (45) (40.23g, 73%), m.p. 292-293°C (lit.[27] m.p. 292-293°C).

ii. cis-3-Thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarboxylic acid 3,3-dioxide (68)

A suspension of cis-3-thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarboxylic anhydride 3,3-dioxide (45) (29.78g, 0.138 mol) in water (120 ml) was stirred and heated under reflux for 10 min, by which time a colourless solution containing a small quantity of charred solid was realised. Removal of the latter by hot filtration under reduced pressure, followed by evaporation in vacuo gave, as a colourless solid, cis-3-thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarboxylic acid 3,3-dioxide (68) (31.84g, 99%), m.p. 187-191°C (lit.[27] m.p. 194-195°C).

iii. cis-3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63)

To dry pyridine (150 ml) (which had been oxygen-saturated by oxygen ebullition for 20 min) stirred and maintained at 67°C was added cis-3-thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarboxylic acid

3,3-dioxide (68) (21.00g, 89.4 mmol), followed by vacuum-dried lead tetraacetate (57.00g, 0.129 mol). After stirring at 67°C for 5 min, gas began to evolve, this ceasing after a further 8 min. The resultant dark brown solution was added to 15% w/w nitric acid solution (1600 ml). This process was repeated a further four times, and the five aqueous solutions were combined and extracted with methylene chloride (5x1300 ml), the extracts combined and washed with 80% saturated sodium hydrogen carbonate solution (2000 ml), then saturated sodium chloride solution (2000 ml), dried over anhydrous magnesium sulphate and the dried filtrate evaporated in vacuo to generate a brown semi-crystalline mass. Following sublimation at 100°C, 0.1 mm Hg, a colourless solid, cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) (11.00g, 17%), m.p. 68-72°C (lit.[34] m.p. 71-72°C), was obtained.

b. Preparation of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a)

i. From cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63)

A solution of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) (7.16g, 49.7 mmol) and maleic anhydride (5.43g, 55.4 mmol) in acetone (200 ml) was irradiated using a 100W lamp, through a quartz immersion well, for 4.5 days. The colourless crystals formed were filtered off, and the acetone filtrate reduced to small volume, the resultant colourless solid precipitate filtered off, washed with ether, and added to the original product giving (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a) (8.15g, 68%), m.p. (decomp.) 286-287°C. Further purification by sublimation at 200-250°C, 0.7 mm Hg gave colourless needles, m.p. (decomp.) 288-290°C.

EA: $C_{10}H_{10}O_5S$ requires 49.6% C, 4.2% H; found 49.4% C, 4.1% H; ^{1}H NMR (CD_3SOCD_3; 200 MHz) δ [ppm]: 2.82 (bd s; 2H), 3.09-3.55 (m; 6H), 3.67 (d, J = 1.7 Hz; 2H); ^{13}C NMR (CD_3SOCD_3; 25 MHz) and ^{13}C DEPT NMR (CD_3SOCD_3; 90.6 MHz) δ [ppm]: 38.69 (CH), 42.08 (CH), 45.52 (CH), 53.51 (CH_2), 173.39 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1843 and 1776 (anhydride C=O), 1303 (SO_2), 1252, 1171, 1136 (SO_2), 1084, 955, 918, 711; MS [EI] m/e (%): 243 (1; $(M+1)^+$), 170 (2), 150 (6), 106 (34), 105 (30), 91 (94), 81 (100), 78 (66).

ii. From cyclobut-3-ene-cis-1,2-dicarboxylic anhydride (244)

α. Cyclobut-3-ene-cis-1,2-dicarboxylic anhydride (244)

An adaptation of the experimental procedure described by Bloomfield et al[113] was used. A solution of maleic anhydride (32.00g, 0.327 mol) and benzophenone (12.50g, 68.7 mmol) in ethyl acetate (350 ml) was maintained at -78°C and irradiated through pyrex using a 400W lamp, with acetylene ebullition, for 25h. On warming to room temperature, a small quantity of solid present was removed by filtration, and the filtrate was evaporated in vacuo to give a brown waxy solid. This was distilled and the fraction b.p. 132-142°C, 12 mm Hg retained and recrystallised from diisopropyl ether to give long needle crystals of cyclobut-3-ene-cis-1,2-dicarboxylic anhydride (244) (17.56g, 43%), m.p. 90-92°C (lit.[226] m.p. 89°C).

β. Attempted preparation of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a)

A solution of cyclobut-3-ene-cis-1,2-dicarboxylic anhydride (244) (128 mg, 1.03 mmol) and butadiene sulphone (134 mg, 1.14 mmol)

in acetone (6 ml) was irradiated through quartz using a 100W lamp for 75h. Evaporation of the resultant solution gave a yellow oil (375 mg), which on ^{1}H NMR analysis was found to contain none of the title compound (242a) (by comparison with the ^{1}H NMR spectrum of an authentic sample of (242a)); only minor quantities of both starting materials were identified.

Similar results were obtained on irradiation of the following solutions, containing the stated photosensitiser, through quartz glassware using a 100W lamp for the period of time indicated:

(a) Anhydride (244) (0.492g, 3.97 mmol), butadiene sulphone (0.473g, 4.01 mmol), benzophenone (72 mg, 0.40 mmol) in ethyl acetate (20 ml) for 62h.

(b) Anhydride (244) (0.272g, 2.19 mmol), butadiene sulphone (0.274g, 2.32 mmol), benzophenone (0.268g, 1.47 mmol) in acetone (20 ml) for 16h.

(c) Anhydride (244) (0.250g, 2.02 mmol), butadiene sulphone (0.246g, 2.08 mmol), acetophenone (0.120g, 1.00 mmol) in acetone (20 ml) for 48h.

c. Preparation of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo [5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208)

i. (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (243)

A mixture of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a) (7.38g, 30.5 mmol) in water (40 ml) was heated under reflux

for 45 min and the resultant solution cooled and evaporated in vacuo to give a colourless solid, (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (243) (7.85g, 99%). Further purification by recrystallisation from water gave cubic crystals (6.82g, 86%) which on heating to 225-230°C were observed to undergo dehydration back to anhydride (242a), m.p. 286-287°C.

EA: $C_{10}H_{12}O_6S$ requires 46.2% C, 4.6% H; found 46.0% C, 4.6% H; ^{1}H NMR (CD_3SOCD_3; 200 MHz) δ [ppm]: 2.76 (s; 2H), 3.11-3.47 (bd m; 6H), 3.49 (d, J = 1.4 Hz; 2H), acid protons not visible; ^{13}C NMR (CD_3SOCD_3; 25 MHz) and ^{13}C DEPT NMR (CD_3SOCD_3; 90.6 MHz) δ [ppm]: 38.54 (CH), 40.01 (CH), 45.53 (CH), 53.74 (CH_2), 173.61 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 3144 (carboxylic acid OH), 1736 and 1692 (acid C=O), 1350, 1294 (SO_2), 1251, 1198, 1127 (SO_2), 1094, 945, 882, 832, 690; MS [EI] m/e (%): 261 (0.1; $(M+1)^+$), 243 (1), 170 (3), 150 (13), 106 (40), 105 (45), 98 (29), 91 (92), 81 (100), 78 (62).

ii. (cis-1-transoid-1,2-cis-2)-4-Thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208)

To dried pyridine (150 ml), pre-saturated with oxygen by ebullition of the gas for 20 min, stirred at 67°C was added (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (243) (7.25g, 27.9 mmol) followed by vacuum-dried lead tetraacetate (19.50g, 44.0 mmol). On stirring at 67°C the orange mixture began to evolve gas after 2 min; after a further 5 min this had ceased. The resultant dark brown solution was added to 12% nitric acid solution (1450 ml) and this extracted with methylene chloride (5x250 ml), the extracts combined, washed with 80% saturated sodium hydrogen carbonate solution (350 ml), then with

saturated sodium chloride solution (350 ml), dried over anhydrous magnesium sulphate and the dried filtrate reduced *in vacuo* to give a brown solid (2.04g). Sublimation of this at 120°C, 0.05 mm Hg gave pure (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (1.64g, 35%) as a colourless solid, identical in all respects to that obtained previously by a different route.

B. Preparation of (cis-1-cisoid-1,2-cis-2)-4-Thiatricyclo[5.2.0.$0^{2,6}$]-non-8-ene 4,4-dioxide (209)

1. Attempted preparation from reaction of cyclobutadiene with butadiene sulphone

a. Using cyclobut-3-ene-cis-1,2-dicarboxylic anydride (244)

To a stirred solution of butadiene sulphone (0.610g, 5.17 mmol) in oxygen-saturated, dry pyridine (10 ml) at 67°C was added cyclobut-3-ene-cis-1,2-dicarboxylic anhydride (244) (0.312g, 2.52 mmol) and lead tetracetate (1.731g, 3.91 mmol). On stirring at 67°C for 1 min, the dark brown mixture proceeded to evolve gas which ceased some 3 min later. Addition of the mixture to 12% nitric acid solution (120 ml), followed by extraction of the resultant red aqueous solution with methylene chloride (5x35 ml), washing of the combined extracts with 80% saturated sodium hydrogen carbonate solution (80 ml) and then saturated sodium chloride solution, drying over anhydrous magnesium sulphate, and evaporation in vacuo of the dried filtrate gave light brown crystals of butadiene sulphone (0.510g; 84% recovered), identified by ^{1}H NMR spectroscopy and by comparison of TLC (silica; ether) with an authentic sample.

b. Using cyclobutadiene iron tricarbonyl (253)

i. Preparation of cyclobutadiene iron tricarbonyl (253)

α. Dimethyl cis/trans-3,4-dichlorotricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene-7,8-dicarboxylate (251)

This was prepared following the procedure of Pettit et al[124], an adaptation of the original method of Avram et al[227]. A solution of cyclooctatetraene (10.00g, 96.1 mmol) in dry carbon tetrachloride (30 ml) was maintained at -30°C during slow ebullition

of dry chlorine gas (6.90g, 97.3 mmol uptake) over a 45 min period. On warming to room temperature, powdered sodium carbonate was added and the mixture shaken well for 5 min, filtered, and to the filtrate was added dimethyl acetylenedicarboxylate (DMAD) (12.90g, 90.8 mmol). The resultant solution was heated under reflux for 3h, cooled and evaporated *in vacuo* to give, as a light yellow oil, dimethyl cis/trans-3,4-dichlorotricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene-7,8-dicarboxylate (251) (31.28g; 100% = 30.48g), ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.70-2.82 (m; 2H), 3.67-3.92 (m; 8H), 4.14-4.30 (m; 2H), 6.55 (dd, J = 4.2 Hz, 3.6 Hz; 2H). TLC (silica; ether) analysis indicated the presence of two main components, R_f 0.58 and 0.68, in accord with two isomeric products.

β. cis-3,4-Dichlorocyclobut-1-ene (252)

Large scale FVP [130°C, 475°C, 9×10^{-3} mm Hg] of dimethyl cis/trans-3,4-dichlorotricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene-7,8-dicarboxylate (251) (28.16g, 88.8 mmol) over a 10h period gave a light brown liquid pyrolysate. On distillation, two colourless fractions were obtained: the first, b.p. *ca* 60°C at 40 mm Hg, was identified by ^{1}H NMR spectroscopy as a mixture of (E,Z)- and (E,E)-1,4-dichlorobuta-1,3-dienes (2.45g, 22%); the second, b.p. 70-80°C at 40 mm Hg, was found to comprise a mixture of cis-3,4-dichlorocyclobut-1-ene (252) (est. 2.09g, 19%) [^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 5.15 (t, J = 1.5 Hz; 2H), 6.27 (t, J = 1.5 Hz; 2H)] and (E,Z)- and (E,E)-1,4-dichlorobuta-1,3-dienes (est. 0.70g, 6%), following ^{1}H NMR and GLC (10% PEGA, 100°C) analyses. This material was used in the next stage without further purification.

γ. Cyclobutadiene iron tricarbonyl (253)

The procedure of Paquette and Wisel25 was utilised. A solution of cis-3,4-dichlorocyclobut-1-ene (252) (2.79g '75%' =

2.09g 100%, 17.0 mmol - remaining 25% (E,Z)- and (E,E)-1,4-dichlorobuta-1,3-dienes) in n-hexane (40 ml) was stirred at 50°C during the addition, in 17 equal portions over an 8h period, of diiron enneacarbonyl (18.50g, 50.9 mmol). The decrease in concentration of (252) was followed by GLC analysis (10% PEGA, 100°C) which indicated completion of reaction after stirring at 50°C for a further 3.5h; the concentration of the impurities was not found to have decreased in this time. After filtration of the brown solid present, the filtrate was evaporated *in vacuo* to give a green semi-solid residue. Distillation of this gave a forerun of iron pentacarbonyl, b.p. *ca* 20°C at 16 mm Hg, followed by cyclobutadiene iron tricarbonyl (253) (1.58g, 48%) as a green liquid, b.p. 65-70°C at 16 mm Hg (lit.[125] b.p. 45-47°C, 3 mm Hg), ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.93 (s; 4H) [lit.[123] ^{1}H NMR δ 3.95 (s; 4H)].

ii. Attempted preparation of (cis-1-cisoid-1,2-cis-2)-4-thia-tricyclo[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (209)

The general method of cyclobutadiene generation described by Warrener *et al*[136] was followed. A solution of cyclobutadiene iron tricarbonyl (253) (0.202g, 1.05 mmol) and butadiene sulphone (0.127g, 1.08 mmol) in ethanol (30 ml) was stirred vigorously at 0°C during the addition of ceric ammonium nitrate (4.160g, 7.59 mmol) in a single portion. Evolution of gas began immediately with this subsiding after a few minutes. After stirring at 0°C for a further 10 min, the red-coloured mixture was poured into iced water (60 ml) and the resultant solution extracted with methylene chloride (3x30 ml). Evaporation of the combined extracts gave a red oil which was dissolved in methylene chloride (50 ml), washed with water (2x20 ml), dried over anhydrous magnesium sulphate and the dried filtrate evaporated to give a crystalline residue (141 mg). Analysis of this by 1H NMR

spectroscopy and TLC (silica; ether) indicated that only recovered butadiene sulphone was present.

2. From dimethyl cis-bicyclo[2.2.0]hex-5-ene-endo-cis-2,3-dicarboxylate (256)

a. Preparation of dimethyl cis-bicyclo[2.2.0]hex-5-ene-endo/exo-cis-2,3-dicarboxylates (256)/(260)

i. Dimethyl cis-bicyclo[2.2.0]hex-5-ene-endo-cis-2,3-dicarboxylate (256)

The reaction conditions used were based on those described by Schmidt[126] for a related synthesis. A solution of cyclobutadiene iron tricarbonyl (253) (0.514g, 2.68 mmol) and maleic anhydride (0.508g, 5.18 mmol) in 'superdry' methanol (40 ml) was vigorously stirred at 0°C under a nitrogen atmosphere and ceric ammonium nitrate (10.40g, 19.0 mmol) added in a single portion. Brisk evolution of gas ensued which ceased after some 30s; after stirring at 0°C for a further 10 min, concentrated sulphuric acid (0.08 ml) was added and the mixture heated under reflux for 1h. On cooling, the mixture was evaporated *in vacuo* to yield a red solid to which was added methylene chloride (60 ml) and water (60 ml) with complete dissolution of the solid. The organic layer was separated and the aqueous phase extracted with further methylene chloride (4x20 ml), the organic fractions combined, dried over anhydrous magnesium sulphate and the dried filtrate evaporated to reveal a mobile, light yellow oil (0.886g).

TLC analysis (silica; ether) indicated a single product spot, coincidental with dimethyl maleate (R_f 0.63), to be present. However, NMR and GLC (10% PEGA, 170°C) analyses indicated the product to comprise an equimolar mixture of dimethyl maleate (est. 360 mg) and dimethyl cis-bicyclo[2.2.0]hex-5-ene-endo-cis-2,3-dicarboxylate (256) (est. 0.526 g, 100% from (253)).

(256): ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.38-3.60 (m; 4H), 3.63 (s; 6H), 6.28 (bd s; 2H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 41.16, 42.21, 51.15, 138.72, 171.53 (Q); MS [EI] m/e (%): 196 (4; M^+), 165 (12), 137 (38), 113 (97), 105 (45), 99 (47), 93 (44), 91 (41), 78 (40), 77 (88), 59 (100); GLC (10% PEGA, 170°C): t_R 24.0 min (cf. dimethyl cis-bicyclo[2.2.0]hex-5-ene-exo-cis-2,3-dicarboxylate (260) described immediately below, t_R 20.1 min under identical GLC conditions).

Due to the difficulties of chromatographic (other than GLC) separation, the unresolved mixture was used in the next reaction stage without further purification.

ii. Dimethyl cis-bicyclo[2.2.0]hex-5-ene-exo-cis-2,3-dicarboxylate (260)

A suspension of cis-1-transoid-1,2-cis-2-bicyclo[2.2.0]-hex-5-ene-exo-cis-2,3-dicarboxylic anhydride (214) (13 mg, 0.087 mmol) in A.R methanol (5 ml) containing concentrated sulphuric aid (3 mg) was heated under reflux for 1.75h. On cooling, the resultant solution was evaporated to small volume, methylene chloride (5 ml) added, the solution again evaporated to small volume and further methylene chloride (5 ml) added. The solution was washed with 80% saturated sodium hydrogen carbonate solution (5 ml), dried over anhydrous magnesium sulphate and the dried filtrate evaporated to dryness giving, as a colourless oil, dimethyl cis-bicyclo[2.2.0]hex-5-ene-exo-cis-2,3-dicarboxylate (260) (13 mg, 77%).

^{1}H NMR ($CDCl_3$; 80 MHz δ [ppm]: 3.17 (t, J = 1.5 Hz; 2H), 3.52-3.75 (m; 8H), 6.39 (t, J = 1.5 Hz; 2H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 42.61, 44.38, 51.66, 141.93, 172.98 (Q); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2949, 1740, 1433, 1352, 1321, 1269, 1237,

1192, 1154, 1053, 940, 761; MS [EI] m/e (%): 196 (4; M^+), 181 (3), 165 (24), 149 (13), 137 (30), 105 (54), 93 (82), 91 (64), 78 (62), 77 (100); GLC (10% PEGA, 170°C): t_R 20.1 min.

b. endo-cis-Bis(hydroxymethyl)-cis-bicyclo[2.2.0]hex-5-ene (257)

A solution of dimethyl cis-bicyclo[2.2.0]hex-5-ene-endo-cis-2,3-dicarboxylate (256) (est. 0.731g, 3.73 mmol) and dimethyl maleate (est. 0.537g, 3.73 mmol) in dry tetrahydrofuran (70 ml) was added dropwise, over a 30 min period, to a stirred suspension of lithium aluminium hydride (1.193g, 31.4 mmol) in dry tetrahydrofuran (30 ml) under nitrogen. The mixture was then heated under reflux, under nitrogen, for 2h before being cooled to room temperature and the excess of lithium aluminium hydride destroyed by sequential addition of water (1.5 ml) in tetrahydrofuran (10 ml), 15% sodium hydroxide solution (2 ml), and water (1 ml). After filtration of the colourless inorganic salts and thorough washing of these with further tetrahydrofuran, the combined filtrates were evaporated to dryness and methylene chloride (30 ml) added. The resultant solution was dried over anhydrous magnesium sulphate and the dried filtrate evaporated in vacuo to give a light yellow oil (0.649g), a mixture of butan-1,4-diol (est. 0.254g, 76% from dimethyl maleate) - identified by comparison of ^1H and ^{13}C NMR spectra with a commercially available sample - and endo-cis-bis(hydroxymethyl)-cis-bicyclo[2.2.0]hex-5-ene (257) (est. 0.395g, 76%).

^1H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.20-3.75 (bd m; 10H), 6.18 (t, J = 1.5 Hz; 2H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.19 (CH), 42.34 (CH), 62.00 (CH_2), 139.36 (CH); MS [EI] m/e (%): 140 (4; M^+), 107 (10), 92 (21), 91 (43), 79 (100), 77 (42), 71 (36), 57 (31).

As the two component mixture could not be resolved under a variety of TLC conditions, it was used in the next reaction step without further purification.

c. endo-cis-2,3-Bis(p-toluenesulphonyloxymethyl)-cis-bicyclo [2.2.0]hex-5-ene (258)

A suspension of p-toluene sulphonyl chloride (6.94g, 36.4 mmol) in pyridine (20 ml) was stirred at 0°C during the dropwise addition, over a 1h period, of a solution of butan-1,4-diol (est. 0.254g, 2.82 mmol) and endo-cis-bis(hydroxymethyl)-cis-bicyclo[2.2.0]-hex-5-ene (257) (est. 0.395g, 2.82 mmol) in pyridine (20 ml). After stirring at 0°C for a further 3h, the red product solution was poured into iced water (300 ml), 10% hydrochloric acid solution added until the aqueous phase was slightly acidic and the orange solid present filtered off and washed with water. Following azeotropic evaporation to dryness with acetone, the resultant powder was recrystallised from ethanol to give colourless crystals (1.295g), found by TLC (silica; 50:50 petroleum-ether (b.p. 40-60°C):ether) analysis to comprise two UV-active components R_f 0.23 and 0.18.

Repeated MPLC [silica; petroleum-ether (b.p. 40-60°C) → 50:50 petroleum-ether (b.p. 40-60°C):ether; 15 psi (1.0 kg cm^{-2})] allowed separation of the two components:

(a) R_f 0.23, endo-cis-2,3-bis(p-toluenesulphonyloxymethyl)-cis-bicyclo[2.2.0]hex-5-ene (258) (0.543g, 43% from (257)) as colourless plates, m.p. 118.5-120°C, on recrystallisation from ethanol.

EA: $C_{22}H_{24}O_6S_2$ requires 58.9% C, 5.4% H; found 59.1% C, 5.4% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.43 (s; 6H), 2.78-2.91 (sym m; H_2, H_3), 3.24 (bd d, $J_{1,2}(J_{3,4})$ = 5.1 Hz; H_1,H_4), 3.84-4.05 (cm; 4H), 6.04 (t, $J_{1,6}(J_{4,5}) = J_{1,5}(J_{4,6})$ = 1.2 Hz; H_5,H_6), 7.32 and 7.72 (A_2B_2 pattern, J = 8.2 Hz; 8H) - assignments made on the basis of selective ^{1}H NMR decoupling studies; ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 21.41, 34.69, 42.14, 68.71, 127.67 (2xCH), 129.75 (2xCH), 133.10 (Q),

139.70, 144.72 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1596, 1490, 1349 (SO_2), 1188, 1162 (SO_2), 1096, 953, 853, 831, 815, 787, 754, 678, 657; MS [CI: NH_3] m/e (%): 466 (9; $[M+18\ (NH_4)]^+$), 434 (6), 416 (3), 312 (15), 277 (9), 139 (22), 123 (41), 104 (66), 91 (78), 78 (31), 35 (100).

(b) R_f 0.18, 1,4-bis(p-toluenesulphonyloxymethyl)butane (0.258g, 23% from butan-1,4-diol) as colourless fingers, m.p. 77-77.5°C (lit.[127] m.p. 83°C), on recrystallisation from ethanol.

d. (cis-1-cisoid-1,2-cis-2)-4-Thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene (259)

i. Using aqueous ethanol as solvent

To a solution of endo-cis-2,3-bis(p-toluenesulphonyloxymethyl)-cis-bicyclo[2.2.0]hex-5-ene (258) (0.174g, 0.389 mmol) in ethanol (15 ml) was added, with stirring, a solution of sodium sulphide nonahydrate (0.291g, 1.21 mmol) in water (15 ml). The resultant mixture was stirred and heated under reflux for 3h: TLC (silica; 50:50 petroleum-ether (b.p. 40-60°C):ether) analysis indicated the absence of (258), R_f 0.23, although no products were apparent.

The reaction solution was evaporated to dryness and the residue dissolved on addition of water (20 ml) and methylene chloride (20 ml). Following separation of the latter, the aqueous layer was extracted with methylene chloride (3x15 ml), the organic fractions combined, dried over anhydrous magnesium sulphate and the dried filtrate reduced in vacuo to give a yellow oil (23 mg). ^1H NMR analysis indicated this to be a complex mixture of products containing little or none of the desired product (259).

ii. Using anhydrous HMPA as solvent

The general procedure described by Paquette et al[105] was employed. A mixture of sodium sulphide nonahydrate (0.543g, 2.26

mmol) in hexamethylphosphoramide (HMPA) (6.0 ml) was dehydrated by distillation of a fraction (1.2 ml) up to b.p. 120°C, 12 mm Hg. On cooling, the blue anhydrous solution of sodium sulphide in HMPA was decanted from the residual solid material present and added to endo-cis-2,3-bis(p-toluenesulphonyloxymethyl)-cis-bicyclo[2.2.0]hex-5-ene (258) (0.213g, 0.475 mmol). On stirring of the resultant blue/green solution at ambient temperature for 17h, TLC (silica; ether) indicated the absence of ditosylate (258) (R_f 0.66) and presence of a product, R_f 0.87. Water (20 ml) was added to the reaction solution and the whole extracted with ether (5x15 ml), the extracts combined, washed with water (3x25 ml) and dried over anhydrous magnesium sulphate. Evaporation of the dried filtrate gave a mobile light yellow oil (65 mg) containing unidentified materials together with (cis-1-cisoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene (259) (est. 32.5 mg, 50%).

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.67-3.65 (m; 8H), 6.31 (s; 2H); ^{13}C DEPT ($CDCl_3$; 50.3 MHz) δ [ppm]: 35.92 (CH_2), 41.31 (CH), 45.38 (CH), 139.85 (CH); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2955, 2923, 1437, 1318, 1282, 1228, 1150, 1126, 1038, 909, 779, 748, 707; MS [EI] m/e (%): 138 (49; M^+), 123 (12), 105 (22), 92 (30), 91 (81), 84 (53), 79 (14), 78 (33), 77 (23), 60 (100).

In light of the potentially high losses involved in purification of the small quantity of product obtained, the crude material was used in the next reaction stage without further purification.

e. (cis-1-cisoid-1,2-cis-2)-4-Thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (209)

A solution of (cis-1-cisoid-1,2-cis-2)-4-thiatricyclo[5.2.0.02,6] non-8-ene (259) (51 mg est. 50% w/w pure = 25.5 mg 100%, 0.185 mmol) in

dry methylene chloride (3 ml) was stirred at 0°C during the dropwise addition, over 10 min, of a solution of m-chloroperoxybenzoic acid (161 mg '85%' = 137 mg 100%, 0.793 mmol) in dry methylene chloride (9 ml). After stirring at room temperature for 70h, TLC (silica; ether) indicated that no starting material (259) (R_f 0.87) remained and a single product spot (R_f 0.47), coincidental with the transoid sulpholane (208), was detected. The product solution was washed with 80% saturated sodium carbonate solution (3x20 ml), dried over anhydrous magnesium sulphate and evaporated to give a light yellow oil. Following preparative TLC (silica; ether), the single product spot (R_f 0.47) was obtained, realising pure (cis-1-cisoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (209) (20 mg, est. 64% yield from (259); 32% from ditosylate (258)) as a colourless oil which on cooling yielded crystals, m.p. 32-36°C.

EA: $C_8H_{10}O_2S$ requires 56.4% C, 5.9% H; found 56.1% C, 6.1% H; ^{1}H NMR ($CDCl_3$; 360 MHz) δ [ppm]: 2.81-2.90 (sym m; H_{3b},H_{5b}), 3.07-3.15 (sym m; H_{3a},H_{5a}), 3.25-3.32 (sym m; H_2,H_6), 3.47-3.50 (sym m; H_1,H_7), 6.39 (dist. dd, $J_{1,8}(J_{7,9})$ = 1.7 Hz, $J_{1,9}(J_{7,8})$ = 1.4 Hz; H_8, H_9). Assignment of signals to protons were made on the basis of ^{1}H NOE difference NMR spectra, and following selective ^{1}H NMR decoupling studies which allowed quantification of coupling constants: $J_{1,2}(J_{6,7})$ = 5.0 Hz, $J_{1,6}(J_{2,7})$ = 2.5 Hz, $J_{1,8}(J_{7,9})$ = 1.7 Hz, $J_{1,9}(J_{7,8})$ = 1.4 Hz, $J_{2,3a}(J_{5a,6})$ = 7.2 Hz, $J_{2,3b}(J_{5b,6})$ = 6.2 Hz, $J_{2,5a}(J_{3a,6})$ = 2.2 Hz, $J_{2,5b}(J_{3b,6})$ = 2.3 Hz, $J_{3a,3b}(J_{5a,5b})$ = 13.1 Hz; ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 32.25 (CH), 44.14 (CH), 52.61 (CH_2), 140.63 (CH); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2965, 1402, 1297 (SO_2), 1270, 1227, 1136 (SO_2), 1087, 974, 941, 914, 897, 868, 785; MS [EI] m/e (%): 170 (20; M+), 105 (95), 104 (51), 92 (42), 91 (100), 79 (85), 78 (98), 77 (68), 65 (49), 52 (56), 51 (61).

C. Cyclobutene Reactivity of (cis-1-transoid-1,2-cis-2)-4-Thiatricyclo [5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208)

1. Reaction with 1,3-dipoles

a. With p-anisonitrile oxide (264)

i. Generated by base elimination of hydrogen chloride from p-anisohydroxamic chloride (269)

A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (0.203g, 1.19 mmol) and p-anisohydroxamic chloride[228] (269) (0.437g, 2.36 mmol) in benzene (5 ml) was stirred during the dropwise addition, over a 5h period, of a solution of triethylamine (0.244g, 2.42 mmol) in benzene (9 ml). After stirring for 16h, the fine light yellow precipitate was filtered off, washed well with water, then acetone, and dried in vacuo to give 6-(p-methoxyphenyl)-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-4-oxa-11-thia-5-azatetracyclo[7.3.0.$0^{2,8}0^{3,7}$]dodec-5-ene 11,11-dioxide (270a) (0.314g, 82%), m.p. (decomp.) 271-273°C.

EA: $C_{16}H_{17}NO_4S$ requires 60.2% C, 5.4% H, 4.4% N; found 60.0% C, 5.4% H, 4.1% N; ^{1}H NMR (CD_3SOCD_3; 200 MHz) δ [ppm]: 2.70-2.82 (m; 2H), 3.07-3.52 (m; 6H), 3.79 (s; 3H), 4.51 (dd, $J_{3,7}$ = 6.1 Hz, $J_{7,8}$ = 1.0 Hz; H_7), 5.19 (d, $J_{3,7}$ = 6.1 Hz; H_3), 6.99 and 7.55 (A_2B_2 pattern, J = 8.9 Hz; 4H); ^{13}C NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 35.16, 38.12, 44.56, 47.80, 53.45, 53.71, 54.96, 55.25, 83.55, 114.39 (2xCH), 120.33 (Q), 128.32 (2xCH), 157.19 (Q), 160.67 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1604, 1513, 1353, 1301 (SO_2), 1250, 1173, 1135 (SO_2), 1094, 1019, 858, 827; MS [EI] m/e (%): 319 (17; M^+), 290(6), 254(11), 194(8), 186(10), 175(100), 147(12), 132(5), 91(35), 77(23).

ii. Generated by thermal elimination of hydrogen chloride from p-anisohydroxamic chloride (269)

A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (0.1084g; 0.638 mmol) and p-anisohydroxamic chloride[328] (269) (0.1197g, 0.645 mmol) in dry toluene (10 ml) was heated under reflux for 40h, by which time evolution of hydrogen chloride had ceased. On cooling, the brown crystals present were filtered off and dried to give 6-(p-methoxyphenyl)-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-4-oxa-11-thia-5-azatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodec-5-ene 11,11-dioxide (272a) (39.4 mg, 19%), identical in all respects to that described above. Evaporation of the filtrate gave a brown oil, separated by preparative TLC (silica; ether) into two fractions. The first fraction (R_f ca 0.60) was obtained as a yellow oil (26.0 mg) found by ^{1}H NMR spectroscopy to contain only aromatic signals; the second fraction (R_f ca 0.39) was obtained as a brown oil (22.0 mg) found by ^{1}H NMR spectroscopy to be an equimolar mixture of recovered olefin (208) (10%) and cis-8-thia-bicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (10%).

b. With C,N-diphenyl nitrone (265)

A mixture of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (0.200g, 1.18 mmol) and C,N-diphenyl nitrone[229] (265) (0.250g, 1.27 mmol) in dry benzene (10 ml) was heated under reflux for 24h at which time TLC (silica; ether) monitoring indicated the absence of olefin (208). On cooling, a little brown solid (11 mg) present was removed by filtration, the filtrate reduced by evaporation in vacuo to small volume before being cooled to -20°C and allowed to warm to room temperature. The resultant precipitated solid was filtered off, washed well with ether and

recrystallised from diisopropyl ether/methylene chloride giving 5,endo-6-diphenyl-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-4-oxa-11-thia-5-azatetracyclo[7.3.0.0^{2,8}0^{3,7}]dodecane 11,11-dioxide (271a) (0.214g, 50%) as fine colourless needles, m.p. 158-161°C.

EA: $C_{21}H_{21}NO_3S$ requires 68.6% C, 5.8% H, 3.8% N; found 68.4% C, 6.0% H, 3.6% N; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.40 (dt, $J_{2,8}$ = 4.7 Hz, $J_{7,8}$ = $J_{8,9}$ = 1.3 Hz; H_8), 2.82-3.33 (cm; 7H - includes 2.96 (dd, $J_{2,8}$ = 4.7 Hz, $J_{1,2}$ = 1.1 Hz; H_2)), 3.56 (ddd, $J_{6,7}$ = 6.8 Hz, $J_{3,7}$ = 5.1 Hz, $J_{7,8}$ = 1.3 Hz; H_7), 4.44 (d, $J_{6,7}$ = 6.8 Hz; H_6), 4.86 (d, $J_{3,7}$ = 5.1 Hz; H_3), 6.99-7.35 (cm; 10H) - assignments made on the basis of ^{1}H-2D COSY and NOESY NMR spectra; ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 35.06 (CH), 37.52 (CH), 38.12 (CH), 46.77 (CH), 54.21 (CH_2), 54.56 (CH_2), 57.80 (CH), 69.73 (CH), 80.75 (CH), 119.35 (2xCH), 123.76 (CH), 127.48 (CH), 127.65 (2xCH), 128.34 (2xCH), 128.55 (2xCH), 136.44 (Q), 148.64 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1492, 1452, 1308 (SO_2), 1254, 1139 (SO_2), 1103, 752, 697; MS [EI] m/e (%): 367 (10; M^+), 338 (1), 303 (0.3), 286 (3), 274 (1), 262 (2), 249 (1), 235 (100), 234 (100), 220 (18), 181 (32), 143 (10), 104 (16), 91 (13), 77 (19).

c. With diazomethane (266)

i. Preparation of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-11-thia-4,5-diazatetracyclo[7.3.0.0^{2,8}0^{3,7}]dodec-4-ene 11,11-dioxide (272a)

To a solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208) (0.240g, 1.41 mmol) in methanol (20 ml) was added a solution of diazomethane (266) (est. 0.59g, 14.0 mmol) in ether (20 ml) [prepared using the procedure of Vogel[230]. The resultant solution was kept at 0-3°C for 4.5 days, by which time

the yellow colouration associated with diazomethane had disappeared. TLC (silica; ether) analysis indicated that starting olefin (208) was still present, and so further of the solution of diazomethane (est. 0.15g, 3.57 mmol) in ether (5 ml) was added. After maintaining the reaction mixture at 0-3°C for a further 3 days, TLC analysis indicated the absence of olefin (208) and the yellow (excess diazomethane) mixture was evaporated to small volume. Filtration and washing with methanol/ether, followed by drying in vacuo gave (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-11-thia-4,5-diazatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodec-4-ene 11,11-dioxide (272a) (0.207g, 69%) as large almond-shaped crystals, m.p. (decomp.) > 155°C.

EA: $C_9H_{12}N_2O_2S$ requires 50.9% C, 5.7% H, 13.2% N; found 50.7% C, 6.0% H, 13.4% N; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.28 (dt, $J_{2,8}$ = 4.8 Hz, $J_{7,8}$ = $J_{8,9}$ = 1.4 Hz; H_8), 2.60 (dddd, $J_{6a,7}$ = 8.6 Hz; $J_{3,7}$ = 5.0 Hz, $J_{6b,7}$ = 3.0 Hz, $J_{7,8}$ = 1.4 Hz; H_7), 2.83 (dt, $J_{2,8}$ = 4.8 Hz, $J_{1,2}$ = $J_{2,3}$ = 1.5 Hz; H_2), 2.93-3.36 (cm; H_9, H_{10a}, H_{10b}, H_{12a}, H_{12b}), 3.48-3.57 (m; H_1), 4.54 (ABX_2 pattern: dist dt, $J_{6a,6b}$ = 18.3 Hz, $J_{3,6b}$ = $J_{6b,7}$ = 3.0 Hz; H_{6b}) and 4.71 (ABXY pattern: dist ddd, $J_{6a,6b}$ = 18.3 Hz, $J_{6a,7}$ = 8.6 Hz, $J_{3,6a}$ = 1.5 Hz; H_{6a}), 5.35 (ddt, $J_{3,7}$ = 5.0 Hz, $J_{3,6b}$ = 3.0 Hz, $J_{2,3}$ = $J_{3,6a}$ = 1.5 Hz; H_3) - assignments made on the basis of ^{1}H NMR decoupling experiments; ^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 34.43 (CH), 36.93 (CH), 38.46 (CH), 44.77 (CH), 45.52 (CH), 53.61 (CH_2), 53.70 (CH_2), 83.51 (CH_2), 91.79 (CH); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1540, 1301 (SO_2), 1283, 1252, 1176, 1138 (SO_2), 1114, 1102, 913, 726, 695; MS [EI] m/e (%): 213 (5; $(M+1)^+$), 148 (3), 120 (10), 119 (6), 118 (11), 106 (100), 92 (66), 80 (48), 78 (35), 68 (83).

ii. Preparation of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo[7.1.0.0^{2,8}.0^{3,7}]decane 5,5-dioxide (278; X=CH_2)

A solution of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-11-thia-4,5-diazatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodec-4-ene 11,11-dioxide (272a) (0.275g, 1.30 mmol) in acetonitrile (50 ml) was irradiated through quartz glassware using a 100W lamp for 18h. The product solution was evaporated to dryness, chloroform (20 ml) added and a little insoluble solid (11 mg) filtered off. Evaporation of the filtrate in vacuo gave a light yellow oil (0.305g), separated into two component bands by preparative TLC (silica; ether).

The first band (R_f 0.43) was obtained as a colourless crystalline solid, identified as (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo[7.1.0.0^{2,8}.0^{3,7}]decane 5,5-dioxide (278; X=CH_2) (77 mg, 32%), recrystallised to give cubes, m.p. 130-132°C, from diisopropyl ether/ methylene chloride (6:1) (76% recovery).

EA: $C_9H_{12}O_2S$ requires 58.7% C, 6.6% H; found 58.5% C, 6.5% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 0.43 (dt, $J_{10a,10b}$ = 5.2 Hz, $J_{1,10a}$ = $J_{9,10a}$ = 1.3 Hz; H_{10a}), 0.82 (q, $J_{1,10b}$ = $J_{9,10b}$ = $J_{10a,10b}$ = 5.2 Hz; H_{10b}), 1.70 (ddd, $J_{1,10b}$ ($J_{9,10b}$) = 5.2 Hz, $J_{1,2}$ ($J_{8,9}$) = 2.9 Hz, $J_{1,10a}$ ($J_{9,10a}$) = 1.3 Hz; H_1, H_9), 2.37 (dd, $J_{1,2}$ ($J_{8,9}$) = 2.9 Hz, $J_{2,3}$ ($J_{7,8}$) = 0.8 Hz; H_2, H_8), 2.90-3.45 (cm; 6H) - assignments made on the basis of selective ^{1}H NMR decoupling studies; ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 11.69 (CH_2), 17.79 (2xCH), 37.60 (2xCH), 44.03 (2xCH), 54.78 (2xCH_2); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1303 (SO_2), 1256, 1230, 1188, 1142, 1121 (SO_2), 1089, 893, 867, 749, 689; MS [EI] m/e (%): 185 (2; $(M+1)^+$), 184 (1; M^+), 170 (1), 120 (35), 119 (34), 118 (35), 105 (76), 91 (84), 79 (100), 77 (66).

The second band (R_f 0.26) was isolated as a light yellow oil, identified as an equimolar mixture of exo-7-vinyl-cis-3-thia-

bicyclo[3.2.0]heptane-exo/endo-6-carbaldehyde 3,3-dioxide (279) (40 mg, 15%), which was found to undergo partial polymerisation on standing at room temperature for a few days.

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.82-3.45 (m; 7H), 3.50-3.72 (m; 1H), 4.96-5.27 (m; 2H), 5.60-6.15 (m; 1H), 9.65 (s; 1H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 28.91 (CH), 32.65 (CH), 35.30 (CH), 36.23 (CH), 43.54 (CH), 44.34 (CH), 49.37 (CH), 49.75 (CH_2), 51.31 (CH), 53.39 (CH_2), 54.09 (CH_2), 54.33 (CH_2), 116.11 (CH_2), 117.94 (CH_2), 134.69 (CH), 137.32 (CH), 199.69 (CH), 200.37 (CH); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2935, 1713, 1636, 1411, 1305 (SO_2), 1242, 1137 (SO_2), 996, 920, 732; MS [EI] m/e (%): 200 (1; M^+), 184 (1), 171 (1), 167 (3), 149 (9), 135 (8), 134 (8), 121 (13), 108 (14), 107 (19), 105 (18), 91 (53), 85 (49), 83 (94), 79 (99), 67 (54), 54 (100).

In a control experiment, a solution of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-11-thia-4,5-diazatetracyclo[7.3.0.0^{2,8}.0^{3,7}]-dodec-4-ene 11,11-dioxide (272a) (11 mg, 0.052 mmol) in freshly dried d_3-acetonitrile (1.0 ml), through which had been bubbled dry nitrogen for 20 mins, was placed in a quartz NMR tube and photolysed using a 100W lamp with continuous nitrogen ebullition. ^{1}H NMR analysis after irradiation for 5h indicated the complete consumption of starting material (272a), the presence of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo[7.1.0.0^{2,8}.0^{3,7}]decane 5,5-dioxide (278; X=CH_2) (est. 4 mg, 42%) and complete absence of the aldehyde isomers (279).

d. With ozone (267)

i. Preparation of cis-3-thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarboxylic acid 3,3-dioxide (68)

A similar oxidative work-up of the ozonide to that described by

Bailey [231] was employed. A stream of ozone (267) in oxygen, generated using a standard ozonolyser, was passed through a solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208) (30.6 mg, 0.18 mmol) in methanol (4 ml), which was cooled to -78°C, for a period of 15 min by which time excess ozone was present in solution, as evidenced by a blue colouration. This was confirmed by the formation of iodine in an acidified potassium iodide solution trap attached to the reaction vessel outlet. The excess of ozone in solution was removed by continued oxygen ebullition and on warming to room temperature, evaporation in vacuo gave a residue of colourless oil (47 mg). A solution of hydrogen peroxide (0.14 ml 30% hydrogen peroxide solution, 1.24 mmol) in formic acid (0.35 ml 90% solution) was added and the resultant solution heated at 90°C for 2h. On cooling, the product solution was evaporated to give a light yellow solid (37 mg) which on trituration with acetone/ether gave cis-3-thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarboxylic acid 3,3-dioxide (68) (14 mg, 33%) as a colourless powder, m.p. 182-187°C (lit.[27] m.p. 194-195°C), displaying identical ^{1}H and ^{13}C NMR spectra to a sample prepared by an alternative route (see p.453).

ii. Attempted preparation of cis-3-thiabicyclo[3.2.0]heptane-exo-cis-6,7-dicarbaldehyde 3,3-dioxide (282)

α. Using sodium iodide as ozonide reducing agent

The reaction conditions of Bailey et al [232], used for a related synthesis, were employed. A stream of ozone (267) in oxygen was bubbled through a solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.02,6]non-8-ene 4,4-dioxide (208) (99 mg, 0.58 mmol) in methanol (13 ml) at -78°C for 15 min by which time excess ozone was

present in solution (blue colouration). Excess ozone was removed by oxygen ebullition for 10 min, after which a solution of sodium iodide (133 mg, 0.89 mmol) in acetic acid (5 ml) was added. The resultant solution was allowed to warm slowly to room temperature and after 1h the liberated iodine was removed by washing with 10% potassium thiosulphate solution (6 ml). Following evaporation to small volume in vacuo, methylene chloride (30 ml) and water (20 ml) were added and the organic layer separated. The aqueous layer was extracted with methylene chloride (2x30 ml), the organic fractions combined, dried over anhydrous magnesium sulphate and the dried filtrate evaporated to leave a colourless liquid (41 mg). Analysis of this by ^{1}H NMR spectroscopy indicated that only a small aldehydic signal was present; TLC (alumina; ether) analysis indicated the presence of at least five components.

β. Using catalytic hydrogenation to reduce ozonide

A stream of ozone (267) in oxygen was bubbled through a solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (82 mg, 0.48 mmol) in dry ethyl acetate (20 ml), maintained at -78°C. After 8 min the solution became deep blue in colour (excess ozone present) and ebullition using purely oxygen was continued for 30 min. Thereafter the colourless solution was allowed to warm to room temperature with dry nitrogen ebullition; TLC (silica; ether) analysis of the product solution indicated the absence of starting olefin (208).

The ozonide solution was added to pre-reduced platinum oxide (Adam's catalyst) (21 mg) in dry ethyl acetate (10 ml) and the mixture stirred vigorously under hydrogen (1 atmosphere pressure) for 3h by which time hydrogen uptake had ceased at 127% of theoretical. On filtration of the catalyst, followed by washing with ethyl acetate,

the filtrate and washings were evaporated *in vacuo* to give a colourless solid. This was washed with methylene chloride, with the washings on evaporation yielding a colourless oil (28 mg), found by ^{1}H NMR spectroscopy to contain only saturated resonances. After drying, the colourless solid (89 mg) was analysed by ^{1}H and ^{13}C DEPT NMR spectroscopy and found to contain no aldehydic signals. This material appeared to comprise of a *ca* 2:1 ratio of two saturated, non-symmetrical C_8 sulphone structures, but identification of these was not achieved.

e. *With ethyl azidoformate (268)*

A mixture of (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (210 mg, 1.24 mmol) and ethyl azidoformate (268) (166 mg, 1.44 mmol) in dry carbon tetrachloride (15 ml) was heated under reflux, forming a solution after a short time. After heating for 30h, the reaction solution was cooled and reduced *in vacuo* to give a residue of brown oil, found to display three separate components on analysis by TLC (silica; ether). Separation of these was achieved by flash chromatography (silica; ether) giving:

(a) R_f 0.52, a colourless crystalline solid identified as *endo*-8-chloro-*exo*-9-(trichloromethyl)-(*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (291) (12 mg, 3%), m.p. 171-173°C on recrystallisation from methylene chloride/diisopropyl ether (69% recovery on recrystallisation).

EA: $C_9H_{10}Cl_4O_2S$ requires 33.4% C, 3.1% H; found 33.6% C, 3.0% H; *^{1}H NMR ($CDCl_3$; 250 MHz) δ [ppm]*: 2.81 (ddd, $J_{1,7}$ = 5.1 Hz, $J_{7,8}$ = 3.4 Hz, $J_{7,9}$ = 0.8 Hz; H_7), 3.02-3.20 (cm; 4H including H_1,H_2), 3.25-3.38 (cm; 2H), 3.58 (ddd, $J_{8,9}$ = 7.0 Hz, $J_{7,8}$ = 3.4 Hz, $J_{1,8}$ =

0.7 Hz; H_8), 3.81 (tdd, J = 7.9, 2.9, 2.0 Hz; H_6), 4.82 (ddd, $J_{1,9}$ = 7.9 Hz, $J_{8,9}$ = 7.0 Hz, $J_{7,9}$ = 0.8 Hz; H_9) - assignments made on the basis of information from ^1H - 2D COSY and NOESY, and 2D ^1H-^{13}C correlated NMR spectra; ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 32.62 (CH), 39.49 (CH), 39.74 (CH), 41.34 (CH), 53.88 (CH), 54.17 (CH_2), 54.48 (CH_2), 70.59 (CH), 98.38 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1299 (SO_2), 1256, 1196, 1135 (SO_2), 1116, 932, 897, 840, 798, 785, 761, 706, 692; MS [EI] m/e (%): 327 (7; [M($2x^{35}Cl$, $2x^{37}Cl$) + 1]$^+$), 325 (23), 323 (30), 291 (11), 289 (33), 287 (32), 253 (3), 251 (3), 225 (5), 223 (9), 221 (5), 207 (4), 205 (12), 137 (17), 135 (23), 90 (35), 88 (100), 85 (10), 83 (13).

(b) R_f 0.46, a colourless solid, found to be starting olefin (208) (149 mg; 71% recovered) by ^1H NMR spectroscopy.

(c) R_f 0.10, a colourless viscous oil, identified as ethyl (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thia-10-azatetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane-10-carboxylate 5,5-dioxide (290) (26 mg, 8%).

^1H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.20 (t, J = 7.1 Hz, CH_3), 2.69 (d, $J_{1,2}(J_{8,9})$ = 3.3 Hz; H_2, H_8), 2.89-3.19 (m; 6H), 3.23 (d, $J_{1,2}(J_{8,9})$ = 3.3 Hz; H_1, H_9), 4.12 (q, J = 7.1 Hz; CH_2); ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 14.25 (CH_3), 34.87 (2xCH), 39.14 (2xCH), 45.85 (2xCH), 54.15 ($2xCH_2$), 62.43 (CH_2), 159.49 (Q); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2930, 1723 (CO), 1372, 1302 (SO_2), 1234, 1188, 1141 (SO_2), 1118, 1095, 730, 696; MS [EI] m/e (%): 257 (2; M^+), 212 (2), 191 (3), 170 (3), 149 (14), 139 (100), 120 (13), 118 (14), 105 (26), 104 (21), 91 (69), 80 (75), 67 (77).

A control experiment was performed in which a mixture of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.02,6]non-8-ene 4,4-

dioxide (208) (26 mg) in dry carbon tetrachloride (2 ml, same batch as that used above) was heated under reflux for 64h. Evaporation *in vacuo* of the cooled solution gave quantitative recovery of starting olefin (208) (26 mg). ^{1}H NMR spectroscopy and TLC (silica; ether) analysis confirmed that tetrachloride (291) was absent, and the formation of this product in the immediately preceeding experiment is therefore dependent on the presence of ethyl azidoformate (268).

2. Diels-Alder reactions

a. With 1,3-diphenylisobenzofuran (292)

A solution of (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo-[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208) (0.105g, 0.618 mmol) and 1,3-diphenylisobenzofuran (292) (0.172g, 0.637 mmol) in dry benzene (10 ml) was heated under reflux, under an atmosphere of nitrogen, for 5h by which time the deep green/yellow colouration associated with the diene had almost disappeared. On cooling, the product solution was evaporated to dryness and the residue triturated with diisopropyl ether. The solid present was filtered off and recrystallised from methylene chloride/diisopropyl ether to give *cis*-1,11-diphenyl-(*cis*-2-*transoid*-2,3-*cis*-3-*transoid*-3,4-*cis*-4)-12,13-benzo-14-oxa-6-thia-pentacyclo[9.2.1.0^{2,10}.0^{3,9}.0^{4,8}]tetradec-12-ene 6,6-dioxide (293) (0.213 g, 78%) as slightly yellow finger-shaped crystals, m.p. 152.5-154.5°C.

EA: $C_{28}H_{24}O_3S$ requires 76.3% C, 5.5% H; found 76.1% C, 5.5% H; *^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]*: 2.29 (bd s; H_3, H_9), 2.76-3.25 (m; 8H), 6.95-7.20 (m; 4H), 7.31-7.70 (m; 10H); *^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]*: 37.90, 38.60, 51.45, 54.47, 90.21 (Q), 118.80, 126.50 (2xCH), 126.86, 127.71, 128.44 (2xCH), 135.92 (Q), 146.68 (Q); *IR (nujol) $\nu_{max.}$ [cm-1]*:

1398, 1298 (SO_2), 1243, 1175, 1136, 1128 (SO_2), 1093, 982, 890, 761, 743, 700, 668; MS [EI] m/e (%): 440 (0.2; M^+), 422 (0.2), 376 (2), 335 (3), 322 (3), 283 (15), 271 (34), 270 (100), 269 (23), 241 (28), 239 (21), 215 (15), 202 (11), 193 (16), 165 (28), 105 (29), 91 (28), 77 (30).

b. With tetraphenylcyclopentadienone (294)

A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (99 mg; 0.582 mmol) and tetraphenylcyclopentadienone (294) (227 mg; 0.591 mmol) in dry benzene (10 ml) was heated under reflux for 18h, by which time TLC (silica; ether) monitoring indicated the absence of starting olefin (208) (R_f 0.46) and the presence of a UV-active product, R_f 0.35. On cooling, the product solution was evaporated in vacuo to give a purple-coloured crystalline mass. This was triturated with ether giving a slightly purple solid which was recrystallised from methylene chloride/diisopropyl ether to give colourless crystals, m.p. 192-225°C, of a ca 2:1 mixture of endo/exo-14-oxo-1,11,12,13-tetraphenyl-(cis-1-cisoid/transoid-1,2-cis-2-transoid-2,3-cis-3-transoid-3,4-cis-4)-6-thiapentacyclo-[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]tetradec-12-ene 6,6-dioxide (295a)/(295b) (185 mg, 57%). The isomers could not be separated by prepatative TLC (silica; ether) as they were coincidental at R_f 0.35; however, using this technique a second crop (45 mg - total 230 mg, 71%) of the isomeric mixture was obtained from the combined trituration and recrystallisation filtrates.

EA: $C_{37}H_{30}O_3S$ requires 80.1% C, 5.4% H; found 80.2% C, 5.4% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.47 (bd s; H_3, H_9), 2.85-3.72 (cm; 8H), 6.65-7.20 (m; 20H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.17 (2 x mj), 39.34 (mi), 43.09 (mi), 45.23 (mi), 47.37 (mj), 54.31 (mj), 54.87 (mi), 64.50 (mi), 66.02 (mj), 126.92, 127.11, 127.22, 127.46,

128.06, 128.21, 129.44, 129.70, 130.14, 132.73 (mj), 133.85 (mj), 134.74 (mi), 135.64 (mi), 142.42 (mi), 143.23 (mj), 198.11 (mi CO), 201.19 (mj CO) [mj = major, mi = minor isomers]; IR (nujol) $\nu_{max.}$[cm^{-1}]: 1779 (CO), 1496, 1457, 1305 (SO_2), 1248, 1136 (SO_2), 1099, 770, 752, 732, 700; MS [EI] m/e (%): M^+ not apparent, highest 526 (32; $(M-CO)^+$), 462 (31), 408 (100), 382 (93), 289 (14), 265 (13), 229 (20), 178 (24), 152 (16); MS[CI(NH_3)]: $(M+NH_4)^+$ not apparent, highest m/e 544 ($(M+NH_4-CO)^+$).

3. Reaction with carbenoids and nitrenes

a. With methylene carbenoid

i. Generated by cuprous chloride catalysed decomposition of diazomethane (266)

A similar procedure for the production of a methylene carbenoid to that described by Kirmse et al[139] was employed. A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4-4-dioxide (208) (57 mg, 0.34 mmol) in superdry methanol (8 ml) was maintained at 0-3°C and cuprous chloride (7 mg, 0.07 mmol) added, followed by a solution of diazomethane (266) (est. 0.14g, 3.33 mmol) in ether[230] (5 ml) which was added in six equal portions at 2 min intervals. Upon each addition, the yellow colour associated with diazomethane (266) disappeared after ca 20 sec, with evolution of gas observed. Following completion of addition, the solid catalyst was filtered off and the filtrate reduced in vacuo to give a residue of light green oil (64 mg). Analysis of this by ^1H NMR spectroscopy indicated only the presence of starting olefin (208).

ii. Generated by rhodium acetate catalysed decomposition of diazomethane (266)

To a solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo [5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (0.254g, 1.49 mmol) in

superdry methanol (11 ml) at 0-3°C was added rhodium (II) acetate dimer (21 mg, 0.05 mmol) followed by a solution of diazomethane (266) (est. 0.10g, 2.38 mmol) in ether[230] (8 ml). The catalyst immediately changed in colour from green to red, and the reaction solution also became light red in colour. After standing for 3 days at 0-3°C, the solid present was filtered off, the filtrate evaporated *in vacuo* and the residue sublimed at 140°C, 0.05 mm Hg to give a quantitative recovery of pure starting olefin (208), as evidenced by ^{1}H NMR analysis of the sublimed material.

b. With ethoxycarbonyl nitrene (303)

i. Generated from ethyl p-nitrobenzenesulphonoxycarbamate (301)

α. Under homogeneous reaction conditions

The conditions described by Lwowski and Maricich[141] were used. To a solution of (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo-[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208) (100 mg, 0.588 mmol) and ethyl *p*-nitrobenzenesulphonoxycarbamate ['Lwowski's reagent'] (301) (171 mg, 0.590 mmol) in dry methylene chloride (5 ml) stirred at 0°C under a nitrogen atmosphere was added, dropwise over a 15 min period, a solution of triethylamine (61 mg, 0.604 mmol) in dry methylene chloride (2.5 ml). The resultant solution was stirred at room temperature for 3h, methylene chloride (15 ml) added and the reaction solution washed with water (4x20 ml), dried over anhydrous magnesium sulphate and the dried filtrate evaporated *in vacuo* to give a semi-crystalline residue (151 mg). Analysis of this by ^{1}H NMR spectroscopy revealed that the only sulphone-containing material present was starting olefin (208); comparison of the ^{1}H NMR spectrum with that of

an authentic sample of the aziridine (290) indicated none of the latter to be present. Following flash chromatography (silica; ether), the olefin (208) (67 mg, 67%) was recovered. A small quantity of non-sulphone-containing nitrene by-products (10 mg) of high R_f value was also obtained.

β. Under phase-transfer reaction conditions

This was carried out under similar conditions to those of Seno *et al*[144] for generation of ethoxycarbonyl nitrene. A solution of (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (52 mg, 0.31 mmol), ethyl *p*-nitrobenzenesulphonoxy-carbamate (301) (85 mg, 0.29 mmol) and benzyl triethylammonium chloride (10 mg, 0.04 mmol) in methylene chloride (4 ml) was combined with a solution of sodium hydrogen carbonate (77 mg, 0.92 mmol) in water (2 ml) and the two immiscible layers stirred vigorously for 26h at room temperature. The organic layer was separated and the aqueous layer extracted with methylene chloride (2x5 ml), the organic fractions combined, dried over anhydrous magnesium sulphate and the dried filtrate thus obtained reduced *in vacuo* to give a sweet-smelling colourless oil (63 mg).

Analysis of the ^{1}H NMR spectrum of the product and comparison with the spectra of authentic samples allowed identification of starting olefin (208) (est. 34 mg, 65% recovered (non-isolated) yield) and ethyl (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thia-10-aza-tetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane-10-carboxylate 5,5-dioxide (290) (est. 21 mg, 27%).

4. Miscellaneous reactions

a. Photochemical reactivity

i. With ethyl azidoformate (268)

α. Neat photolysis

The method of photoexcitation of ethyl azidoformate (268) described by Meyers and Takaya[26] was utilised. An intimate mixture of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (90 mg, 0.53 mmol) and ethyl azidoformate (268) (73 mg, 0.63 mmol) was placed in a quartz tube and irradiated at 400W. Brisk evolution of gas (nitrogen) was observed initially. After irradiation for 3h, evolution of gas appeared to have ceased and the resultant semi-crystalline brown photolysate (129 mg) was analysed by ^{1}H NMR spectroscopy. Both this and TLC (silica; ether) analyses indicated the absence of the aziridine (290), and the only sulphone-containing material detected was the starting olefin (208) which was present in unchanged quantity.

β. Solution photolysis

A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (54 mg, 0.318 mmol) and ethyl azidoformate (268) (38 mg, 0.330 mmol) in carbon tetrachloride (0.35 ml) and chloroform (0.15 ml) was irradiated through quartz using a 100W lamp for 23h. Evaporation of the resultant mixture gave a colourless crystalline solid (54 mg) which was found to be completely soluble in chloroform. Analysis of this material by ^{1}H NMR spectroscopy indicated it to be almost pure starting olefin (208), containing only small quantities of nitrene by-products, none of which appeared to be sulphone-containing.

ii. With maleic anhydride

α. Preparation of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo[7.2.0.$0^{2,8}$.$0^{3,7}$]undecane-exo-cis-10,11-dicarboxylic anhydride 5,5-dioxide (305)

A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (97 mg, 0.57 mmol) and maleic anhydride (67 mg, 0.68 mmol) in acetone (3 ml) was placed in a quartz tube and irradiated with a 100W medium pressure mercury lamp. The progress of reaction was followed by TLC (silica; ether) which indicated complete consumption of starting olefin (208) after irradiation for 22h. Evaporation of the mixture of crystalline solid (which began to form after irradiation for 4h) and acetone solution to half volume, followed by filtration gave colourless crystals (63 mg). A second crop (33 mg) was realised on complete evaporation of the filtrate, trituration of the residue with chloroform followed by filtration of the insoluble solid, and drying. Sublimation of the combined product at 205-210°C, 0.25 mm Hg gave (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo[7.2.0.$0^{2,8}$.$0^{3,7}$]undecane-exo-cis-10,11-dicarboxylic anhydride 5,5-dioxide (305) (70 mg, 46%) as colourless crystals, m.p. 228-231°C.

EA: $C_{12}H_{12}O_5S$ requires 53.7% C, 4.5% H; found 53.5% C, 4.5% H; ^{1}H NMR (CD_3SOCD_3; 80 MHz) δ [ppm]: 2.88 (s; H_2, H_8), 3.02 (s; H_1,H_9), 3.12-3.40 (m; 6H), 3.55 (s; H_{10},H_{11}); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1852 and 1773 (CO anhydride), 1304 (SO_2), 1235, 1132 (SO_2), 1072, 918, 873; MS [EI] m/e (%): 268 (10; M^+), 222 (6), 196 (8), 132 (45), 131 (65), 117 (86), 104 (33), 94 (67), 91 (100).

β. Preparation of dimethyl (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo[7.2.0.0^{2,8}.0^{3,7}]undecane-exo-cis-10,11-dicarboxylate 5,5-dioxide (306)

A mixture of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo[7.2.0.0^{2,8}.0^{3,7}]undecane-exo-cis-10,11-dicarboxylic anhydride 5,5-dioxide (305) (48 mg, 0.179 mmol) and concentrated sulphuric acid (4 mg) in methanol (3 ml) was heated under reflux, forming a solution after 30 min. After 1h, the solution was cooled, evaporated to dryness in vacuo and the residue triturated with ether. The resultant solid was filtered off, washed with further ether, dried in vacuo and then recrystallised from methanol to give dimethyl (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo-[7.2.0.0^{2,8}.0^{3,7}]undecane-exo-cis-10,11-dicarboxylate 5,5-dioxide (306) (35 mg, 62%) as colourless flakes, m.p. 135-137°C.

EA: $C_{14}H_{18}O_6S$ requires 53.5% C, 5.8% H; found 53.3% C, 5.5% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.83 (bd s; H_2,H_8), 3.04-3.28 (m; 8H), 3.41-3.52 (m; 2H), 3.68 (s; 6H); ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz)δ[ppm] : 38.30 (CH), 42.09 (CH), 45.14 (CH), 45.92 (CH), 51.75 (CH_3), 54.82 (CH_2), 172.45 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1738 (CO), 1434, 1358, 1336, 1323, 1306 (SO_2), 1274, 1250, 1221, 1187, 1142, 1127 (SO_2); MS [EI] m/e (%): M^+ not apparent, 283 (30; [M-OMe]$^+$), 254 (8), 222 (15), 195 (12), 190 (7), 158 (8), 131 (33), 125 (100), 97 (24), 93 (76), 91 (35), 59 (54).

b. Hydrogenation

i. Using platinum oxide as catalyst

A suspension of platinum oxide (Adam's catalyst) (22 mg) in dry ethyl acetate (15 ml) was pre-reduced by vigorous stirring under

a pressure of one atmosphere of hydrogen until uptake of hydrogen had ceased. To this was added (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (0.159g, 0.935 mmol) and on complete dissolution of this material the reaction mixture was vigorously stirred under a pressure of one atmosphere of hydrogen until uptake of hydrogen had ceased (after some 2h). The catalyst was filtered off and the filtrate evaporated in vacuo to give a colourless oil. This was distilled at 59-61°C, 0.05 mm Hg, giving a colourless oil which crystallised on trituration with n-hexane. Filtration and drying gave (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (307) (152 mg, 94%) as colourless crystals, m.p. 53-58°C.

EA: $C_8H_{12}O_2S$ requires 55.8% C, 7.0% H; found 55.6% C, 6.8% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.80-2.76 (m; 6H), 2.82-3.34 (m; 6H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 25.96 (CH_2), 40.07 (CH), 40.19 (CH), 54.82 (CH_2); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1397, 1296 (SO_2), 1261, 1233, 1187, 1133 (SO_2), 1103, 902, 699; MS [EI] m/e (%): 173 (5; $(M+1)^+$), 107 (27), 106 (26), 93 (77), 91 (67), 80 (87), 79 (81), 67 (85), 54 (100).

ii. Using palladium-on-charcoal as catalyst

To a solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (107 mg, 0.629 mmol) in 'superdry' ethanol (10 ml) was added 10% palladium-on-charcoal (23 mg) and the resultant mixture hydrogenated in a standard hydrogenation apparatus at slightly greater than one atmosphere of hydrogen. On cessation of hydrogen gas uptake - after some 2.5h - the catalyst was filtered off, washed with further ethanol and the combined filtrate and washings evaporated in vacuo. The residue of colourless oil was identified as an equimolar mixture of (cis-1-transoid-1,2-cis-2)-

4-thiatricyclo[5.2.0.0^{2,6}]nonane 4,4-dioxide (307) and cis-8-thiabicyclo-[4.3.0]nonane 8,8-dioxide (308) (107 mg, 49% each component) by comparison of ^{1}H and ^{13}C NMR spectra with those of authentic samples (the synthesis of (308) is described below). No separation of the two products could be achieved by TLC or by vacuum distillation.

iii. Preparation of cis-8-thiabicyclo[4.3.0]nonane 8,8-dioxide (308)

To a solution of cis-8-thiabicyclo[4.3.0]non-3-ene 8,8-dioxide (65) (0.365g, 2.12 mmol) in 'superdry' ethanol (15 ml) was added 10% palladium-on-charcoal and the mixture hydrogenated at slightly greater than one atmosphere pressure of hydrogen in a standard hydrogenation apparatus. After 2h, uptake of hydrogen had stopped and the catalyst was removed by filtration. Reduction of the filtrate by evaporation in vacuo gave a colourless oil (0.353g) which crystallised on cooling. This was recrystallised from n-hexane/ether to give cis-8-thiabicyclo[4.3.0]nonane 8,8-dioxide (308) (0.303g, 82%) as fine colourless needles, m.p. 38-40°C (lit.[233] m.p. 39-41°C).

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.27-1.74 (m; 8H), 2.41-2.68 (sym m; 2H), 2.91-3.18 (m; 4H); ^{13}C DEPT ($CDCl_3$; 50.3 MHz δ [ppm]: 21.94 (CH_2), 26.41 (CH_2), 36.08 (CH), 56.10 (CH_2); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2930, 2858, 1453, 1413, 1304 (SO_2), 1218, 1134, 1114 (SO_2), 912, 793, 748; MS [EI] m/e (%): 174 (35; M^+), 157 (63), 99 (74), 95 (18), 81 (26), 67 (100), 55 (29), 54 (26).

c. Bromination

A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]non-8-ene 4,4-dioxide (208) (0.185g, 1.09 mmol) in dry methylene chloride (5 ml) was stirred at -78°C during the dropwise addition, over 15 min, of a solution of bromine (0.230g, 1.44 mmol)

in dry methylene chloride (3 ml). Upon initial addition the bromine was instantly decolourised; at a later stage during addition the red colour remained indicating that excess of bromine had been added. Following completion of bromine addition, the resultant red solution was stirred at -78°C for 30 min and then allowed to warm to room temperature.

TLC (silica; ether) analysis indicated the absence of starting olefin (208), R_f 0.46, and presence of a single product spot, R_f 0.50. The excess of bromine and the solvent were removed by evaporation in vacuo giving a light orange oil. Trituration with ether and filtration of the resultant solid gave, after drying in vacuo, a colourless powder, exo-8-endo-9-dibromo-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (309) (0.319g, 89%). Recrystallisation from ethanol gave colourless plates (0.231g, 64%), m.p. 135-136°C.

EA: $C_8H_{10}Br_2O_2S$ requires 29.1% C, 3.0% H; found 28.9% C, 3.0% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.90-3.45 (m; 7H), 3.51-3.89 (m; H_6), 4.50 (dd, $J_{8,9}$ = 6.3 Hz, $J_{7,8}$ = 2.4 Hz; H_8), 4.99 (ddd, $J_{1,9}$ = 7.9 Hz, $J_{8,9}$ = 6.3 Hz, $J_{7,9}$ = 0.8 Hz; H_9); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz δ [ppm]: 34.90 (CH), 39.89 (CH), 44.48 (CH), 47.70 (CH), 51.80 (CH), 52.24 (CH), 53.76 (CH_2), 54.24 (CH_2); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1305 (SO_2), 1242, 1185, 1134 (SO_2), 1106, 947, 893, 773, 718, 689, 610; MS [EI] m/e (%): M^+ not apparent, 251 (14; $(M-Br)^+$), 249 (13; $(M-Br)^+$), 185 (45), 183 (44), 134 (25), 132 (26), 106 (35), 105 (100), 104 (32), 91 (45), 79 (28), 78 (24), 77 (28).

d. Epoxidation

A solution of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208) (0.189g; 1.11 mmol) in acetic

acid (4.35 ml) containing 30% 'w/v' hydrogen peroxide solution (0.87 ml, 7.68 mmol) was stirred and heated at 55-60°C for 26h, by which time TLC (silica; ether) monitoring indicated complete consumption of starting olefin (208) (R_f 0.46) and presence of a product spot (R_f 0.09).

Water (40 ml) was added and sodium hydrogen carbonate added portionwise until further addition resulted in no more evolution of gas. The resultant neutral solution was extracted with methylene chloride (3x50 ml), the extracts combined, dried over anhydrous magnesium sulphate and the dried filtrate thus obtained evaporated *in vacuo* to give a colourless crystalline residue. Recrystallisation from isopropanol/methylene chloride gave (*cis*-1-*transoid*-1,2-*cis*-2-*transoid*-2,3-*cis*-3)-10-oxa-5-thiatetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane 5,5-dioxide (278; X=O) (0.104g) as colourless cubes, m.p. 160-161.5°C. A further batch (31 mg, total 0.135 g, 65%) of pure epoxide was realised on preparative TLC (alumina; methylene chloride) purification of the recrystallisation filtrate.

EA: $C_8H_{10}O_3S$ requires 51.6% C, 5.4% H; found 51.4% C, 5.6% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.77 (dt, $J_{1,2}(J_{8,9})$ = 2.9 Hz, $J_{1,8}$ ($J_{2,9}$) = $J_{2,3}(J_{7,8})$ = 0.7 Hz; H_2,H_8), 2.98-3.16 (cm; 4H), 3.23-3.37 (cm; 2H), 3.99 (dist dd, $J_{1,2}(J_{8,9})$ = 2.9 Hz, $J_{1,8}(J_{2,9})$ = 0.7 Hz; H_1,H_9); ^{13}C NMR (CD_3COCD_3; 25 MHz) δ [ppm]: 33.93, 49.00, 54.08, 54.78; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1301 (SO_2), 1264, 1238, 1135 (SO_2), 1110, 1092, 928, 902, 850, 773, 696; MS [EI] m/e (%): 186 (8; M^+), 122 (7), 121 (8), 107 (10), 103 (24), 91 (42), 77 (52), 68 (100), 53 (84).

e. Addition of a sulphenyl halide

i. With succinimide-N-sulphenyl chloride (310)

The general method of Bombala and Ley[148] was adopted. To a solution of (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-

8-ene 4,4-dioxide (208) (0.250g, 1.47 mmol) in dry methylene chloride (13 ml), stirred at room temperature, was added dropwise, over a 30 min period, a solution of succinimide-N-sulphenyl chloride (310) (0.366, 2.21 mmol) in dry methylene chloride (7 ml). After stirring at ambient temperature for a further 1h, TLC (silica; ether) analysis indicated the absence of starting olefin (208) and the reaction solution was evaporated *in vacuo* to give a yellow semi-solid residue. Treatment of this with ether gave a colourless solid (465 mg) which was filtered off, washed with further ether and dried *in vacuo*. Recrystallisation from methylene chloride/diisopropyl ether gave *endo*-8-chloro-*exo*-9-(succinimidothio)-(*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (312) (0.311g, 63%) as colourless crystals, m.p. 146-147°C.

EA: $C_{12}H_{14}ClNO_4S_2$ requires 42.9% C, 4.2% H, 4.2% N; found 42.7% C, 4.2% H, 4.1% N; ^{1}H NMR (CD_2Cl_2; 200 MHz) δ [ppm]: 2.57 (dd, $J_{1,7}$ = 4.7 Hz, $J_{7,8}$ = 3.5 Hz; H_7), 2.83 (s; 4H), 2.98-3.35 (m; 6H), 3.69-3.81 (sym cm; H_6), 3.88 (dd, $J_{8,9}$ = 6.8 Hz, $J_{7,8}$ = 3.5 Hz; H_8), 4.78 (dd, $J_{1,9}$ = 7.8 Hz, $J_{8,9}$ = 6.8 Hz; H_9) - assignments made on the basis of selective decoupling studies; ^{13}C NMR (CD_2Cl_2; 50.3 MHz) δ [ppm]: 28.29 (2xCH_2), 32.98, 39.95, 41.09, 44.38, 54.47, 54.82, 58.68, 59.20, 176.52 (2xQ); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1724 (CO), 1304 (SO_2), 1244, 1140 (SO_2), 1123; MS [EI] m/e (%): 335 (0.4; M^+ (^{35}Cl)), 300 (4), 237 (4), 205 (8), 200 (9), 183 (8), 136 (7), 105 (14), 100 (52), 99 (100).

ii. Preparation of (*cis*-1-*transoid*-1,2-*cis*-2-*transoid*-2,3-*cis*-3)-5,10-dithiatetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane 5,5-dioxide (278; X=S)

A variation of the general procedure described by Bombala and Ley[14] was employed. A solution of *endo*-8-chloro-*exo*-9-(succinimidothio)-(*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (312)

(0.192g, 0.572 mmol) in dry tetrahydrofuran (20 ml) was added dropwise over 45 min to a stirred suspension of lithium aluminium hydride (88 mg, 2.32 mmol) in dry tetrahydrofuran (10 ml) at 0°C. The mixture was stirred at room temperature for 3h and the excess of lithium aluminium hydride destroyed by careful addition of water (3 ml) in tetrahydrofuran (3 ml). After filtration of the inorganic salts, and washing of these with further tetrahydrofuran, the combined filtrate and washings were evaporated in vacuo to give a solid residue. This was dissolved in methylene chloride (20 ml), dried over anhydrous magnesium sulphate and the resultant dried filtrate evaporated under reduced pressure to give a colourless solid (128 mg). Recrystallisation from methanol gave (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5,10-dithiatetracyclo[7.1.0.0^{2,8}.0^{3,7}]decane 5,5-dioxide (278; X=S) (56 mg, 48%) as colourless squares, m.p. 202.5-203.5°C.

EA: $C_8H_{10}O_2S_2$ requires 47.5% C, 5.0% H; found 47.3% C, 4.9% H; ^{1}H NMR (CD_3COCD_3; 80 MHz) δ [ppm]: 2.66 (dist dd, $J_{1,2}(J_{8,9})$ = 1.8 Hz, $J_{1,8}(J_{2,9})$ = 0.9 Hz; H_2,H_8), 3.09-3.37 (cm; 6H), 3.61 (dist dd, $J_{1,2}(J_{8,9})$ = 1.8 Hz, $J_{1,8}(J_{2,9})$ = 0.9 Hz; H_1,H_9); ^{13}C NMR and ^{13}C DEPT NMR (CD_3COCD_3; 50.3 MHz) δ [ppm]: 34.94 (CH), 36.82 (CH), 49.78 (CH), 53.07 (CH_2); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1302 (SO_2), 1252, 1138 (SO_2), 1109, 1097, 897, 696; MS [EI] m/e (%): 202 (7; M^+), 170 (9), 137 (6), 135 (6), 123 (11), 105 (31), 104 (19), 91 (62), 84 (100).

D. Comparison of transoid (208) and cisoid (209) Isomers of 4-Thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide

1. Bromination of (cis-1-cisoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (209)

a. In methylene chloride solution

A solution of (cis-1-cisoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (209) (21 mg, 0.124 mmol) in dry methylene chloride (2.0 ml) was stirred at room temperature and a few drops of a solution of bromine (30 mg, 0.188 mmol) in dry methylene chloride (1.0 ml) added. No decolourisation of the added bromine was observed after 10s, and the remainder of the bromine solution was added dropwise over a further 50s period. Halfway through the addition the reactant solution became cloudy and an orange solid quickly precipitated. After stirring for a further 1h, the mixture of solid and orange methylene chloride solution was evaporated *in vacuo* and the residue triturated with ether and filtered. The filtrate was reduced *in vacuo* to give purely recovered olefin (209) (8 mg, 38% recovered) as evidenced by ^{1}H NMR analysis; the filtered solid was dried on the sinter yielding 5-bromo-1-oxo-(cis-3-cisoid-3,4-cis-4-cisoid-4,5-cis-5)-10-oxa-1 λ^6-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (336) (38 mg, 99% yield on consumed olefin (209)) as orange crystallites, m.p. (decomp.) 82-84°C.

EA: $C_8H_{10}Br_4O_2S$ requires 19.6% C, 2.1% H; found 17.4% C, 2.0% H; ^{1}H NMR (CD_3CN; 360 MHz) δ [ppm]:- (336) only : 3.31 (overlapping dt, $J_{7,8}$ = 7.6 Hz, $J_{4,7}$ = $J_{6,7}$ = 4.3 Hz; H_7), 3.61 (dd, $J_{5,6}$ = 6.0 Hz, $J_{4,5}$ = 3.0 Hz; H_5), 3.67 (dd, $J_{9a,9b}$ = 15.5 Hz, $J_{2a,9a}$ = 8.7 Hz; H_{9a}), 3.78-3.90 (cm; H_3, H_4, H_8, H_{9b}), 4.17 (ddd, $J_{2a,2b}$ = 16.2 Hz,

$J_{2a,9a}$ = 8.7 Hz, $J_{2a,9b}$ = 1.1 Hz; H_{2a}), 4.43 (dd, $J_{2a,2b}$ = 16.2 Hz, $J_{2b,9b}$ = 1.9 Hz; H_{2b}), 5.91 (dd, $J_{5,6}$ = 6.0 Hz, $J_{6,7}$ = 4.3 Hz; H_6) - spectrum was found to consist of a 40:60 mixture of olefin (209) and salt (336), with the signal to proton, and coupling constant assignments detailed above being made on the basis of selective decoupling studies; Raman (solid) $\nu_{max.}$ [cm^{-1}]: 1107 (w), 1035 (w), 855 (me), 727 (w), 685 (me), 372 (me), 276 (w), 185 (w), 160 (s; Br_3^-), 95 (w); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1372, 1335, 1301, 1281, 1234, 1217, 1109, 1038, 988, 926, 910, 884, 848, 788, 747, 708, 684, 673; MS [positive ion FAB; thioglycerol] m/e (%): 251 (83; $^{81}(M-Br_3)^+$), 249 (81; $^{79}(M-Br_3)^+$), 236 (48), 193 (37), 126 (46), 125 (51), 105 (100), 92 (86), 85 (67), 79 (83), 73 (96); MS [negative ion FAB; benzyl benzoate] m/e (%): 161 (2; $^{81,81}Br_2^-$), 159 (4; $^{79,81}Br_2^-$), 157 (3; $^{79,79}Br_2^-$), 107 (2), 81 (92), 79 (100), 76 (16), 73 (9); MS [CI; ammonia] m/e (%): 350 (29; $^{81,81}(M-Br_2+NH_4)^+$), 348 (61; $^{79,81}(M-Br_2+NH_4)^+$), 346 (27; $^{79,79}(M-Br_2+NH_4)^+$), 270 (24), 268 (33), 264 (15), 251 (13), 249 (12), 231 (9), 188 (100), 105 (22), 91 (24), 78 (14), 70 (8); MS [EI] m/e (%): 330 (4; $^{81,81}(M-Br_2)^+$), 328 (6; $^{79,81}(M-Br_2)^+$), 326 (4; $^{79,79}(M-Br_2)^+$), 251 (83), 249 (82), 185 (94), 184 (85), 171 (19), 170 (43), 169 (21), 157 (32), 134 (100), 132 (100), 119 (17). ^{13}C NMR and UV spectra are described in the following section.

Addition of the tribromide salt (336) (10.0 mg, 0.020 mmol) to d_6-acetone (0.5 ml) resulted in immediate formation of an orange solution which became colourless after a few seconds. Analysis of the resultant solution, to which was added methylene chloride (2.6 mg), by ^1H NMR spectroscopy allowed identification of the sole non-deuterated compound present as the olefin (209) (est. 3.1 mg, 89% from (336)). Comparison of the GLC (5% carbowax; 50°C) analysis of the d_6-acetone

solution with that of a solution of bromine (35 mg) in d_6-acetone (0.5 ml), which had been allowed to stand at room temperature for 30 min, indicated both to contain the same five volatile brominated products in similar ratios.

The unstable nature of the salt (336) was apparent from the release of white fumes observed upon opening of a sealed container in which the salt had been allowed to stand for several hours at room temperature.

b. In d_3-acetonitrile solution

To a solution of (cis-1-cisoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (209) (4.6 mg, 2.7 x 10^{-2} mmol) in d_3-acetonitrile (0.6 ml) was added a solution of bromine in d_3-acetonitrile (61 μl 0.441M; 4.3 mg, 2.7x10^{-2} mmol bromine). ^{1}H NMR spectroscopy indicated the resultant solution to consist of a 60:40 molar ratio of olefin (209) and 5-bromo-1-oxo-(cis-3-cisoid-3,4-cis-4-cisoid-4,5-cis-cis-5)-10-oxa-1 λ^6-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (336). Addition of further of the bromine solution (61 μl 0.441M; 4.3 mg, 2.7x10^{-2} mmol bromine) caused a change in the ratio of (209): (336) to 30:70. It was observed that this ratio was slowly displaced with time in favour of the olefin. Addition of one further molar equivalent of the bromine solution (61 μl 0.441M; 4.3 mg, 2.7x10^{-2} mmol bromine) was found by ^{1}H NMR spectroscopy to result in the presence of solely 5-bromo-1-oxo-(cis-3-cisoid-3,4-cis-4-cisoid-4,5-cis-cis-5)-10-oxa-1 λ^6-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (336): ^{1}H NMR as above; ^{13}C DEPT NMR (CD_3CN; 50.3 MHz) δ [ppm]: 32.62 (CH), 34.77 (CH), 36.12 (CH), 42.88 (CH), 44.58 (CH), 45.12 (CH_2), 48.43 (CH_2), 97.43 (CH); UV (CD_3CN): $\lambda_{max.}$ = 270 nm, $\epsilon_{max.}$ = 22,000.

2. Thermolysis of 5-bromo-1-oxo-(cis-3-cisoid-3,4-cis-4-cisoid-4,5-cis-5)-10-oxa-1 λ^6-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (336)

The title compound (336) (ca 2 mg) was placed on a glass coverslip and positioned on the hot stage of a Reichert hot-stage microscope. Upon heating to 82-84°C, the orange crystallites were observed to melt with formation of an orange liquid which quickly evolved a brown gas before becoming colourless. The resultant colourless oil was cooled and found to be completely soluble in deuteriochloroform, permitting examination of the ^{1}H NMR spectrum. This indicated the absence of olefin (209) or starting material (336), and appeared consistent with the formation of exo-cis-8,9-dibromo-(cis-1-cisoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (339), although this assignment was not further substantiated.

^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 3.25 (dist dd, $J_{1,2}(J_{6,7})$ = 5.7 Hz, $J_{1,9}(J_{7,8})$ = 2.2 Hz; H_1,H_7), 3.35-3.67 (cm; 6H), 5.00 (d, $J_{1,9}(J_{7,8})$ = 2.2 Hz; H_8,H_9).

E. Preparation of Tricyclic and Higher Systems Containing a 4-Thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide Skeleton

1. Preparation of substituted derivatives of 4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242)

a. Preparation of substituted derivatives of cis-3-thiabicyclo[3.2.0]-hept-6-ene 3,3-dioxide (63)

i. Synthesis of 1-methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (341)

α. 1-Methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylic anhydride 3,3-dioxide (343)

This was prepared by the method of Buchan[29]. A solution of 3-methyl-2,5-dihydrothiophene 1,1-dioxide (100) (9.937g, 75.3 mmol) and maleic anhydride (8.162g, 83.3 mmol) in acetone (500 ml) was irradiated through pyrex using a 400W medium pressure mercury lamp for 52h. Reduction of the resultant solution *in vacuo* gave a light yellow oil which on trituration with chloroform/ether and filtration gave 1-methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylic anhydride 3,3-dioxide (343) (6.021g, 35%) as a colourless solid, m.p. 140-148°C (lit.[29] m.p. 157-159°C).

β. 1-Methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylate 3,3-dioxide (344)

A mixture of 1-methyl-*cis*-3-thiabicyclo[3.2.0]heptane-*cis*-6,7-dicarboxylic anhydride 3,3-dioxide (343) (5.884g, 25.6 mmol) in water (20 ml) was heated under reflux with a solution being formed after 5 min. After 20 min, the solution was cooled and evaporated

in vacuo to give a colourless solid (6.123g). This was recrystallised from water to give 1-methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylate 3,3-dioxide (344) (5.473g, 86%) as colourless crystals, m.p. 172-175°C.

EA: $C_9H_{12}O_6S$ requires 43.5% C, 4.9% H; found 43.3% C, 5.0% H; ^{1}H NMR (CD_3SOCD_3; 80 MHz) δ [ppm]: 1.30 (s; 3H), 2.85-3.62 (m; 7H), 12.20-12.60 (bd hump; 2H); ^{13}C NMR (CD_3SOCD_3; 25 MHz) δ [ppm]: 21.97, 40.30, 40.64 (Q), 40.88, 48.89, 55.15, 60.31, 171.73 (Q), 173.10 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 3600-3300 (OH), 1751 (CO), 1687 (CO) 1302 (SO_2), 1164 (SO_2), 912; MS [EI] m/e (%): M^+ not apparent 230 (13; $(M-H_2O)^+$), 212 (4), 203 (4), 185 (7), 148 (14), 138 (38), 121 (22), 99 (96), 94 (72), 93 (97), 79 (100), 77 (56), 68 (64), 53 (47).

γ. 1-Methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (341)

1-Methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylate 3,3-dioxide (344) (5.756g, 23.2 mmol) and lead tetraacetate (15.42g, 34.8 mmol) was added to dry pyridine (70 ml), which had been pre-saturated with oxygen by ebullition for 15 min, and the mixture stirred at intervals while being heated at 67°C. After heating for 2 min, gas evolution started; after a further 5 min, this had ceased and the resultant dark brown solution was added to 10% nitric acid solution (940 ml).

The acidic solution thus obtained was extracted with methylene chloride (5x250 ml), the extracts combined and washed with 80% saturated sodium hydrogen carbonate solution (300 ml), followed by saturated sodium chloride solution (300 ml), dried over anhydrous magnesium sulphate and the dried filtrate evaporated in vacuo to give a brown crystalline residue. TLC (silica; ether) analysis indicated the

presence of the major product, R_f 0.41, and an impurity, R_f 0.22. Column chromatography (silica ; ether) gave the former as a pure colourless crystalline material, identified as 1-methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (341) (0.862g, 24%), obtained as colourless needles, m.p. 73.5-75°C, on recrystallisation from diisopropyl ether/methylene chloride.

EA: $C_7H_{10}O_2S$ requires 53.1% C, 6.4% H; found 53.3% C, 6.6% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.46 (s; 3H), 2.79-3.33 (m; 5H), 6.12 and 6.21 (AB pattern : d, J = 2.7 Hz; 2H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 23.46, 47.54, 49.46 (Q), 53.44, 57.94, 136.31, 143.48; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1313, 1298 (SO_2), 1225, 1212, 1118 (SO_2), 780, 758; MS [EI] m/e (%): 159 (8; $(M+1)^+$), 158 (3; M^+), 141 (1), 94 (85), 93 (81), 91 (100), 79 (97), 78 (88), 77 (100), 64 (62).

ii. Synthesis of 6-methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (342)

α. 6-Methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylic anhydride 3,3-dioxide (345)

The procedure described by Buchan[29] was followed. A solution of butadiene sulphone (20.00g, 0.169 mol) and citraconic anhydride (20.68g, 0.187 mol) in acetone (500 ml) was irradiated through quartz using a 400W lamp for 72h. The crystalline solid (15.05g) present was filtered off, washed with acetone and dried. A second crop was obtained by evaporation of the filtrate to small volume followed by trituration with methylene chloride/ether, giving 6-methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylic anhydride 3,3-dioxide (345) (total 16.76g, 43%) as colourless crystals, m.p. 240-244°C (lit.[29] m.p. 249-250°C).

β. 6-Methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylic acid 3,3-dioxide (346)

A suspension of 6-methyl-cis-3-thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylic anhydride 3,3-dioxide (345) (16.62g, 72.3 mmol) in water (150 ml) was heated under reflux, a solution forming after 10 min. After heating for 30 min, the resultant solution was allowed to slowly cool to ambient temperature and the large colourless crystals present were filtered off, washed with water, then acetone, and dried in vacuo. A second crop was obtained by concentration of the combined filtrate and washings giving 6-methyl-cis-3-thiabicyclo[3.2.0]-heptane-cis-6,7-dicarboxylic acid 3,3-dioxide (346) monohydrate (17.98g, 94%) as colourless crystals. On slow heating, the crystals were found to undergo dehydration at 180-182°C to give rhombic crystals of the corresponding anhydride (345), m.p. 249-250°C (lit.[29] m.p. 249-250°C).

EA: $C_9H_{14}O_7S$ requires 40.6% C, 5.3% H; found 40.8% C, 5.1% H; ^{1}H NMR (CD_3SOCD_3; 80 MHz) δ [ppm]: 1.28 (s; 3H), 2.90-3.55 (m; 9H), 9.0-13.0 (v bd hump; 2H); ^{13}C NMR (CD_3SOCD_3; 25 MHz) δ [ppm]: 18.90, 32.09, 37.67, 47.19, 49.38, 49.98, 53.14, 172.88, 175.79; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 3500 (OH water), 3400-2350 (OH acid), 1723 (CO), 1679 (CO), 1394, 1296 (SO_2), 1253, 1223, 1207, 1187, 1134 (SO_2), 1113, 899, 816, 719; MS [EI] m/e (%): M^+ not apparent 249 (2; $(M-OH)^+$), 230 (16), 203 (8), 185 (7), 184 (6), 158 (19), 138 (9), 110 (9), 94 (26), 79 (100).

γ. 6-Methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (342)

To dry pyridine (300 ml), pre-saturated with oxygen by ebullition for 25 min, stirred at 67°C was added 6-methyl-cis-3-

thiabicyclo[3.2.0]heptane-cis-6,7-dicarboxylic acid 3,3-dioxide (346) monohydrate (17.98g, 67.6 mmol) and lead tetraacetate (48.18g, 108.8 mmol). The mixture became dark brown in colour and after 2 min gas began to evolve with this ceasing after a further 3 min. Addition of the resultant dark brown solution to 12% nitric acid solution (3 litre) gave a clear orange solution which was extracted with methylene chloride (5x500 ml), the extracts combined and washed in turn with 80% saturated sodium hydrogen carbonate solution (800 ml) and saturated sodium chloride solution (800 ml) before being dried over anhydrous magnesium sulphate. Evaporation of the dried filtrate gave a mobile brown oil which was purified by flash chromatography (silica; ether) to give 6-methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (342) (5.489g, 51%) as a colourless oil, b.p. 72-74°C at 0.1 mm Hg, n_D^{21} 1.5059. On cooling in liquid nitrogen followed by slow warming to room temperature, colourless crystals, m.p. 25.5-28.5°C, were obtained.

EA: $C_7H_{10}O_2S$ requires 53.1% C, 6.4% H; found 52.9% C, 6.4% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.62 (dd, J = 1.5 Hz, 0.8 Hz; 3H), 2.71-3.06 (m; 4H), 3.22-3.51 (m; 2H), 5.74 (d, J = 1.5 Hz; 1H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 14.52, 37.49, 42.63, 51.02, 51.75, 130.80, 148.57 (Q); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2936, 1640 (C=C), 1439, 1405, 1302 (SO_2), 1260, 1227, 1128 (SO_2), 1068, 1040, 972, 889, 843, 740, 686; MS [EI] m/e (%): 158 (10; M^+), 94 (11), 93 (13), 91 (14), 79 (100), 77 (41), 65 (9), 53 (35), 51 (33).

b. Photolysis of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) and substituted derivatives with cyclic olefins

i. Photolysis of substituted derivatives of cis-3-thiabicyclo[3.2.0]-hept-6-ene 3,3-dioxide (63) with maleic anhydride

α. 2-Chloro-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (340)

α1. Preparation of 3-chloro-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-cis-8,9-dicarboxylic anhydride 4,4-dioxide (348)

A solution of 2-chloro-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (340)[182] (95 mg, 0.53 mmol) and maleic anhydride (57 mg, 0.58 mmol) in acetone (3 ml) was placed in a quartz tube and irradiated with a 100W lamp. Formation of a colourless solid precipitate was observed after irradiation for 2.5h, and irradiation was stopped after 22h. The solid present was filtered off, washed with acetone and dried in vacuo; a second crop was obtained by concentration of the filtrate to give 3-chloro-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-cis-8,9-dicarboxylic anhydride 4,4-dioxide (348) (104 mg, 71%) as a colourless solid, m.p. 291-292°C.

EA: $C_{10}H_9ClO_5S$ requires 43.4% C, 3.3% H; found 43.2% C, 3.2% H; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1850 and 1774 (CO), 1332, 1322 (SO_2), 1254, 1146 (SO_2), 1072, 952, 903; MS [EI] m/e (%): M^+ not apparent, 241 (1; $(M-Cl)^+$), 206 (1), 204 (3), 186 (2), 184 (5), 149 (5), 142 (3), 141 (4), 140 (10), 139 (9), 125 (7), 117 (18), 115 (46), 105 (85), 91 (88), 81 (100).

α2. Preparation of dimethyl 3-chloro-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-cis-8,9-dicarboxylate 4,4-dioxide (349)

A mixture of 3-chloro-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-cis-8,9-dicarboxylic anhydride 4,4-dioxide (348) (64 mg, 0.23 mmol) and concentrated sulphuric acid (4 mg) in AR methanol (2.5 ml) was heated under reflux for 2h. On cooling, the colourless solid present was filtered off, washed with methanol and then ether, and dried in vacuo to give dimethyl 3-chloro-4-thiatricyclo[5.2.0.$0^{2,6}$]-

nonane-cis-8,9-dicarboxylate 4,4-dioxide (349) (66 mg, 88%) as a granular solid, m.p. 177-179°C.

EA: $C_{12}H_{15}ClO_6S$ requires 44.7% C, 4.7% H; found 44.4% C, 4.5% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.03-3.27 (m; 3H), 3.30-3.57 (m; 5H), 3.67 (s; 6H), 4.66 (s; 1H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.28, 39.33, 39.83, 45.79, 46.47, 49.43, 50.59, 52.03, 52.04, 70.78, 171.42 (2xQ); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1728 and 1710 (CO), 1360, 1341, 1321 (SO_2), 1242, 1217, 1197, 1133 (SO_2), 1098, 1056, 773; MS [EI] m/e (%): M^+ not apparent, 293 (13; $(^{37}M\text{-}OMe)^+$), 291 (32; $(^{35}M\text{-}OMe)^+$), 263 (2), 223 (5), 200 (4), 198 (8), 191 (6), 169 (6), 163 (15), 148 (18), 146 (54), 139 (16), 112 (61), 111 (100), 105 (25), 91 (48), 77 (30).

β. 1-Methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (341)

β1. Preparation of 2-methyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (350)

A solution of 1-methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (341) (0.720g, 4.56 mmol) and maleic anhydride (0.497g, 5.07 mmol) in acetone (100 ml) was irradiated using a 100W lamp for a period of 110h. The product solution was evaporated in vacuo to give a residue of yellow gum to which was added dry ether/dry chloroform. After several days, a colourless solid had formed: this was filtered off and purified by sublimation at 205-210°C, 0.1 mm Hg to give 2-methyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (350) (0.280g, 24%) as a colourless solid, m.p. (decomp.) $>$ 220°C. [This product was found to be very susceptible to hydrolysis, forming the corresponding diacid (351)].

EA: $C_{11}H_{12}O_5S$ requires 51.6% C, 4.7% H; found 51.4% C, 4.6% H; ^{1}H NMR (CD_3SOCD_3; 360 MHz) δ [ppm]: 1.42 (s; 3H), 2.78 (ddd, $J_{1,7}$ = 4.7 Hz, $J_{6,7}$ = 2.3 Hz, $J_{7,8}$ = 1.8 Hz; H_7), 2.88 (dd, $J_{1,7}$ = 4.7 Hz, $J_{1,9}$ = 1.5 Hz; H_1), 3.02 (dt, $J_{5b,6}$ = 8.4 Hz, $J_{5a,6}$ = $J_{6,7}$ = 2.3 Hz; H_6), 3.17 (dd, $J_{3a,3b}$ = 13.9 Hz, $J_{3a,5b}$ = 1.6 Hz; H_{3a}), 3.24 (ddd, $J_{5a,5b}$ = 13.2 Hz, $J_{5a,6}$ = 2.3 Hz, $J_{3b,5a}$ = 1.4 Hz; H_{5a}), 3.35 (dd, $J_{3a,3b}$ = 13.9 Hz, $J_{3b,5a}$ = 1.4 Hz; H_{3b}), 3.49 (ddd, $J_{5a,5b}$ = 13.2 Hz, $J_{5b,6}$ = 8.4 Hz, $J_{3a,5b}$ = 1.6 Hz; H_{5b}), 3.63 (dd, $J_{8,9}$ = 5.3 Hz, $J_{1,9}$ = 1.5 Hz; H_9), 3.70 (dd, $J_{8,9}$ = 5.3 Hz, $J_{7,8}$ = 1.8 Hz; H_8); ^{13}C NMR and ^{13}C DEPT NMR (CD_3SOCD_3; 90.6 MHz) δ [ppm]: 22.32 (CH_3), 39.83 (CH), 41.67 (CH), 42.82 (Q), 44.69 (CH), 45.32 (CH), 45.52 (CH), 54.72 (CH_2), 60.27 (CH_2), 172.79 (Q), 173.90 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1854 and 1775 (CO), 1308 (SO_2), 1251, 1140, 1127 (SO_2), 1068, 940, 906; MS [EI] m/e (%): 256 (2; M^+), 184 (3), 164 (9), 163 (11), 149 (4), 120 (58), 119 (41), 105 (100), 95 (61), 91 (45), 81 (91), 77 (51).

β2. Preparation of 2-methyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (351)

A suspension of 2-methyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (350) (24 mg, 0.094 mmol) in water (0.5 ml) was heated under reflux, with a solution being formed after 15 min. After heating for 1h, the solution was cooled to room temperature with precipitation of a colourless solid. This was filtered off, washed with water and dried *in vacuo* to give 2-methyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (351) (18 mg, 70%) as colourless needles, m.p. 198.5-201°C.

EA: $C_{11}H_{14}O_6S$ requires 48.1% C, 5.1% H; found 47.9% C, 5.1% H; ^{1}H NMR (CD_3SOCD_3; 360 MHz) δ [ppm]: 1.37 (s; 3H), 2.70-2.73 (m; 1H),

2.75-2.81 (m; 2H), 3.10 (dd, J = 13.9Hz, 1.6 Hz; 1H), 3.16 (dd, J = 13.9Hz, 2.8 Hz; 1H), 3.26 (d, J = 13.5 Hz; 1H), 3.35-3.46 (m; 2H), 3.52 (dd, J = 8.9Hz, 2.8 Hz; 1H), 11.4-13.1 (bd hump; 2H); ^{13}C NMR and ^{13}C DEPT NMR (CD_3SOCD_3; 90.6 MHz) δ [ppm]: 21.65 (CH_3), 37.58 (CH), 40.83 (CH), 42.33 (Q), 43.40 (CH), 45.02 (CH), 45.67 (CH), 55.10 (CH_2), 60.80 (CH_2), 173.23 (Q), 173.67 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 3400-2800 (OH), 1727 and 1713 (CO), 1383, 1318 (SO_2), 1227, 1146 (SO_2), 1131; MS [EI] m/e (%): M^+ not apparent, 257 (6; $(M-OH)^+$), 210 (3), 207 (2), 184 (8), 177 (3), 164 (36), 163 (34), 149 (14), 133 (7), 120 (76), 105 (100).

β3. Preparation of dimethyl 2-methyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (352)

A suspension of 2-methyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (350) (88 mg, 0.34 mmol) and concentrated sulphuric acid (15 mg) in AR methanol (5 ml) was heated under reflux for 1h. On cooling, the resultant solution was evaporated in vacuo to give a brown oil, TLC (silica; ether) analysis of which indicated the major component at R_f 0.20, and a minor component at R_f 0.40. Following purification by preparative TLC (silica; ether) the component at R_f 0.20 was isolated as a yellow oil. Microdistillation of this at 190-195°C, 0.15 mm Hg, followed by trituration of the resultant oil with ether gave dimethyl 2-methyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (352) (61 mg, 59%) as colourless rhombic crystals, m.p. 103-105.5°C.

EA: $C_{13}H_{18}O_6S$ requires 51.6% C, 6.0% H; found 51.8% C, 6.1% H; ^{1}H NMR ($CDCl_3$; 360 MHz) δ [ppm]: 1.48 (s; 3H), 2.80 (dt, $J_{5a,6}$ =

8.9 Hz, $J_{5b,6} = J_{6,7}$ = 2.9 Hz; H_6), 2.95 (overlapping dt, $J_{1,7}$ = 5.9 Hz, $J_{6,7} = J_{7,8}$ = 2.9 Hz; H_7), 3.02 (dd, $J_{1,7}$ = 5.9 Hz, $J_{1,9}$ = 3.1 Hz; H_1), 3.04 (dd, $J_{3a,3b}$ = 14.0 Hz, $J_{3a,5a}$ = 1.9 Hz; H_{3a}), 3.09 (ddd, $J_{5a,5b}$ = 14.0 Hz, $J_{5b,6}$ = 2.9 Hz, $J_{3b,5b}$ = 1.0 Hz; H_{5b}), 3.15 (dd, $J_{3a,3b}$ = 14.0 Hz, $J_{3b,5b}$ = 1.0 Hz; H_{3b}), 3.37 (ddd, $J_{5a,5b}$ = 14.0 Hz, $J_{5a,6}$ = 8.9 Hz, $J_{3a,5a}$ = 1.9 Hz; H_{5a}), 3.39 (dd, $J_{8,9}$ = 9.0 Hz, $J_{1,9}$ = 3.1 Hz; H_9), 3.64-3.68 [cm; 7H - includes 3.66 (dd, $J_{8,9}$ = 9.0 Hz, $J_{7,8}$ = 2.9 Hz; H_8) and 3.66 (s; 6H)]; ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 90.6 MHz) δ [ppm]: 22.13 (CH_3), 38.10 (CH), 40.84 (CH), 42.57 (Q), 44.02 (CH), 45.77 (CH), 46.22 (CH), 51.76 (CH_3), 51.80 (CH_3), 55.53 (CH_2), 61.41 (CH_2), 171.66 (Q), 171.99 (Q); IR (nujol) $\nu_{max.}$[cm^{-1}]: 1738 (CO), 1441, 1361, 1303 (SO_2), 1242, 1202, 1161, 1128 (SO_2); MS [EI] m/e (%): 303 (0.3; $(M+1)^+$), 271 (55), 243 (5), 211 (4), 206 (5), 178 (46), 177 (35), 163 (14), 147 (28), 126 (96), 125 (81), 119 (94), 111 (100), 105 (96), 95 (90), 91 (41).

γ. 6-Methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (342)

A solution of 6-methyl-cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (342) (0.141g, 0.89 mmol) and maleic anhydride (99mg, 1.01 mmol) in acetone (4 ml) was irradiated, using a 100W lamp, through quartz for 20h. Evaporation of the reaction solution and trituration of the residue with dry methylene chloride/dry ether gave a colourless solid (0.173g) on filtration. Although IR analysis indicated the presence of anhydride and sulphone groups, this material was found to decompose to give a black solid on attempted sublimation up to 210°C, 0.04 mm Hg.

A suspension of the crude product (78 mg) in methanol (5 ml) containing concentrated sulphuric acid (15 mg) was heated under reflux

for 3h. Evaporation of the resultant mixture followed by trituration of the residue with methylene chloride/ether gave, on filtration, a colourless solid (39 mg). This was found on analysis by IR and ^1H NMR (CD_3SOCD_3 solvent) spectroscopy to be a polymeric ester/sulphone.

Evaporation of the trituration filtrate gave a brown oil which remained at the baseline on TLC (silica; ether) analysis. It was concluded that only polymeric material was obtained from the initial photolysis reaction.

ii. Photolysis of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) with cyclic olefins

α. With N-phenyl maleimide (353)

A solution of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) (0.128 g, 0.89 mmol) and N-phenyl maleimide (353) (92mg, 0.53 mmol) in acetone (4 ml) in a quartz tube was irradiated using a 100W lamp for 21h. The colourless solid present was filtered off and dried in vacuo to give N-phenyl-(cis-1-transoid-1,2-cis-2)-4-thia-tricyclo[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboximide 4,4-dioxide (354) (35 mg, 21%), identified by comparison of ^1H and ^{13}C NMR spectra with those of an authentic sample (see p.510). Evaporation of the acetone filtrate and examination of the residue by ^1H NMR spectroscopy indicated the absence of N-phenyl maleimide (353) or product (354), although a small quantity of starting sulpholane (63) was identified.

β. With cyclopent-4-ene-1,3-dione (355)

A solution of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) (0.146g, 1.01 mmol) and cyclopent-4-ene-1,3-dione (355) (0.107g, 1.11 mmol) in acetone (4 ml) was placed in a quartz tube and irradiated

with a 100W lamp for 6 days. The light brown solid (23 mg) present was filtered off and dried. Examination of this material by ^{1}H NMR and IR spectroscopy indicated it to be a copolymer of both olefinic starting materials. Evaporation of the acetone filtrate gave a viscous yellow oil (0.254g) which was found to comprise mainly of both starting materials (63) and (355).

γ. With cyclohex-2-ene-1,4-dione (356)

A solution of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) (0.108g, 0.75 mmol) and cyclohex-2-ene-1,4-dione (356) (0.100g '90%' [remainder p-benzoquinone], 0.82 mmol) in acetone (5 ml) was placed in a quartz tube and irradiated using a 100W lamp. The course of the reaction was monitored by TLC (silica; ether) which indicated the absence of (356) after irradiation for 48h. A little solid (7 mg) present was removed by filtration: analysis of this by IR spectroscopy indicated that the sulphone group was not present and this material was therefore discarded. Reduction of the filtrate to small volume, followed by addition of chloroform resulted in precipitation of a light yellow solid (0.103g), found to be a copolymer of the two starting materials by ^{1}H and IR spectroscopy; this material was found not to sublime on heating to 220°C at 6 x 10^{-3} mm Hg, in accord with its polymeric nature.

δ. With cyclohex-4-ene-cis-1,2-dicarboxylic anhydride (357)

A solution of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) (98 mg, 0.68 mmol) and cyclohex-4-ene-cis-1,2-dicarboxylic anhydride (357) (0.118g, 0.78 mmol) in acetone (4 ml) was irradiated through quartz using a 100W lamp for 50h, by which time TLC monitoring indicated the absence of olefin (63). Filtration gave a product,

tentatively assigned 6,13-dithiapentacyclo[9.3.0.0^{2,10}.0^{3,9}.0^{4,8}]tetradecane 6,6,13,13-tetraoxide (358) (8 mg, 8%), as colourless crystals, m.p. 272-273°C.

EA: $C_{12}H_{16}O_4S_2$ requires 50.0% C, 5.6% H; found 50.6% C, 5.7% H; ^{1}H NMR (CD_3SOCD_3; 250 MHz) δ [ppm]: 2.63 (s; 4H), 3.03 (d, J = 5.3 Hz; 4H), 3.12 (d, J = 9.3 Hz; 4H), 3.31 (dd, J = 9.3 Hz, 5.3 Hz; 4H); ^{13}C NMR (CD_3SOCD_3; 62.9 MHz) δ [ppm]: 38.02, 44.87, 54.23; IR (nujol) ν max.[cm^{-1}] : 1418, 1408, 1299 (SO_2), 1253, 1207, 1149, 1128 (SO_2), 898, 709, 602; MS [EI] m/e (%): 289 (0.3; $(M+1)^+$), 288 (0.2; M^+), 224 (0.4), 223 (0.5), 170 (0.5), 159 (3), 158 (3), 157 (7), 143 (6), 129 (4), 117 (5), 105 (6), 91 (14), 81 (24), 80 (100), 79 (64).

Evaporation of the filtrate in vacuo gave a polymeric light yellow solid (0.268g).

ε. With butadiene sulphone

A solution of cis-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (63) (93.6 mg, 0.65 mmol) and butadiene sulphone (80.8 mg, 0.68 mmol) in acetone (4 ml) was irradiated through quartz using a 100W lamp for 71h. The colourless solid present was filtered off and dried to give 6,13-dithiapentacyclo[9.3.0.0^{2,10}.0^{3,9}.0^{4,8}]tetradecane 6,6,13,13-tetraoxide (358) (1.2 mg, 1%), identified by comparison of ^{1}H NMR and IR spectra to those of an authentic sample (see above).

2. Preparation of tetracyclic systems from (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a)

a. Preparation of N-phenyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboximide 4,4-dioxide (354)

i. exo-cis-9-(Phenylcarbamoyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-8-carboxylic acid 4,4-dioxide (359)

To a stirred suspension of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a) (0.463g, 1.91 mmol) in methanol (10 ml) was added freshly distilled aniline (0.177g, 1.90 mmol) dropwise over a period of one min. After stirring at room temperature for a further 2.5h, the resultant mixture was filtered and the filtered solid washed with further methanol, followed by ether, and dried at 60°C, 0.1 mm Hg for 2h to give exo-cis-9-(phenylcarbamoyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-8-carboxylic acid 4,4-dioxide (359) (0.541g, 84%) as a colourless powder, m.p. 167-169°C.

EA: $C_{16}H_{17}NO_5S$ requires 57.3% C, 5.1% H, 4.2% N; found 57.2% C, 5.0% H, 4.2% N; ^{1}H NMR (CD_3SOCD_3; 80 MHz) δ [ppm]: 2.73-2.95 (m; 2H), 3.06-3.40 (bd s; 6H), 3.60 (s; 2H), 6.91-7.63 (cm; 5H), 9.83 (bd s; 1H), 11.4-12.7 (v bd hump; 1H); ^{13}C NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 38.31, 38.76, 40.01 (2xCH), 45.01, 48.09, 53.67, 53.88, 119.37 (2xCH), 123.09, 128.53 (2xCH), 139.16, 170.57 (Q), 173.07 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 3340 (NH), 3300-2500 (OH), 1692 (CO), 1651 (CO), 1597, 1535, 1443, 1312 (SO_2), 1254, 1133 (SO_2), 1009; MS [EI] m/e (%): M^+ not apparent, 317 (3; $(M-H_2O)^+$), 240 (10), 194 (3), 170 (7), 150 (4), 133 (6), 119 (5), 106 (35), 105 (23), 93 (100).

ii. N-Phenyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]-nonane-exo-cis-8,9-dicarboximide 4,4-dioxide (354)

A mixture of exo-cis-9-(phenylcarbamoyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane-8-carboxylic acid 4,4-dioxide (359) (0.382g, 1.14 mmol) and sodium acetate (34 mg, 0.41 mmol) in acetic anhydride (4 ml) was stirred and heated at 90-95°C

for 4h. On cooling, the solid present was filtered off, washed with methanol and then with ether, and dried *in vacuo* to give *N*-phenyl-(*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-*exo*-*cis*-8,9-dicarboximide 4,4-dioxide (354) (0.332g, 92%) as a fine colourless powder, m.p. 300-301.5°C.

EA: $C_{16}H_{15}NO_4S$ requires 60.6% C, 4.8% H, 4.4% N; found 60.3% C, 4.7% H, 4.5% N; ^{1}H NMR (CD_3SOCD_3; 80 MHz) δ [ppm]: 2.82 (s; H_1,H_7), 3.10-3.52 (m; 6H), 3.54 (s; H_8,H_9), 7.24-7.61 (cm; 5H); ^{13}C NMR and ^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 38.64 (2xCH), 42.60 (2xCH), 44.76 (2xCH), 53.64 (2xCH_2), 126.90 (2xCH), 128.28 (CH), 128.81 (2xCH), 132.43 (Q), 177.22 (2xQ); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1704 (CO), 1382, 1311, 1298 (SO_2), 1248, 1196, 1157, 1144 (SO_2), 725; MS [EI] m/e (%): 317 (12; M^+), 251 (2), 224 (2), 169 (29), 144 (4), 119 (15), 106 (82), 105 (38), 91 (100), 81 (59), 78 (68).

b. Preparation of (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-*exo*-*cis*-8,9-dicarboxylic thioanhydride 4,4-dioxide (360)

The general procedure of Tamura *et al*[183] was adopted. To powdered (*cis*-1-*transoid*-1,2-*cis*-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-*exo*-*cis*-8,9-dicarboxylic anhydride 4,4-dioxide (242a) (0.751g, 3.10 mmol) was added crushed sodium sulphide nonahydrate (1.115g, 4.65 mmol) and the two solids ground together, forming a grey paste after a few minutes. During the following hour, the paste was remixed at regular intervals and at the end of this period, 20% hydrochloric acid (12 ml) was added with exothermic evolution of gas. On addition of water (25 ml), a cloudy solution was formed and this was extracted with ethyl acetate (5 x 25 ml), the extracts combined, dried over

anhydrous magnesium sulphate and the resultant dried filtrate reduced in vacuo to give a residue of light yellow solid. This was washed with ether, dried in vacuo and then purified by sublimation at 210°C, 6 x 10^{-2} mm Hg to give a colourless solid (0.420g), found by ^{1}H and ^{13}C NMR spectroscopy to consist of a 37:63 mixture of starting anhydride (242a) (est. 0.149g, 20% recovered) and (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic thioanhydride 4,4-dioxide (360) (est. 0.271g, 34% yield). Recrystallisation of a sample of the crude product from ethyl acetate followed by sublimation at 160°C, 8 x 10^{-3} mm Hg gave almost pure thioanhydride (360) (6%) as colourless plates, m.p. (decomp.) 218-220°C, containing only a trace of anhydride (242a) impurity.

EA: $C_{10}H_{10}S_2O_4$ requires 46.5% C, 3.9% H; found 46.7% C, 3.9% H; ^{1}H NMR (CD_3SOCD_3; 200 MHz) δ [ppm]: 2.83 (bd s; 2H), 3.19-3.44 (m; 6H), 3.92 (d, J = 1.3 Hz; 2H); ^{13}C NMR and ^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 38.56 (CH), 43.01 (CH), 53.29 (CH_2), 56.74 (CH), 202.09 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1706 and 1696 (CO), 1302 (SO_2), 1245, 1126 (SO_2), 1098, 1053, 1000, 927, 898, 846, 705, 691, 665; MS [EI] m/e (%): 259 (1; $(M+1)^+$), 256 (1), 198 (3), 170 (24), 150 (4), 133 (4), 106 (56), 105 (38), 91 (100), 81 (24), 79 (31), 78 (59), 77 (26).

c. Preparation of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-oxa-11-thiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 11,11-dioxide (367) and the [10,10,12,12-$^{2}H_4$] derivative (368)

i. Dimethyl (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (365; R=Me)

A mixture of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide

(242a) (0.180g, 0.74 mmol) in methanol (5 ml) containing concentrated sulphuric acid (30 mg) was heated under reflux. After 30 min, a solution was obtained; after 1h, a colourless crystalline precipitate appeared; after 2h, the mixture was cooled to room temperature and filtered. Recrystallisation of the resultant solid from methanol/methylene chloride gave dimethyl (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (365; R=Me) (0.155g, 72%) as fine colourless needles, m.p. 200-201°C.

EA: $C_{12}H_{16}O_6S$ requires 50.0% C, 5.6% H; found 49.8% C, 5.5% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.06 (s; 2H), 3.11-3.30 (m; 6H), 3.53 (d, J = 2.1 Hz; 2H), 3.67 (s; 6H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 39.02, 40.50, 45.94, 51.95, 54.15, 171.77 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1738 and 1714 (CO), 1355, 1303 (SO_2), 1261, 1234, 1200, 1136 (SO_2), 1098, 977, 942, 840, 709; MS [EI] m/e (%): 289 (1; $(M+1)^+$), 257 (61; $(M-OMe)^+$), 229 (5), 164 (41), 112 (100), 111 (73), 105 (99), 97 (63), 91 (41).

ii. Diethyl (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (365; R=Et)

A mixture of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a) (76.0 mg, 0.314 mmol) in absolute ethanol (2 ml) containing concentrated sulphuric acid (20 mg) was heated under reflux for 2h. Upon cooling of the resultant solution, colourless crystals formed and these were filtered off and recrystallised from absolute ethanol to give diethyl (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (365; R=Et) (68.5 mg, 69%) as fine colourless needles, m.p. 146-147°C.

EA: $C_{14}H_{20}O_6S$ requires 53.2% C, 6.4% H; found 53.2% C, 6.2%

H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 1.23 (t, J = 7.2 Hz; 6H), 3.01-3.14 (m; 4H), 3.19-3.32 (m; 4H), 3.51 (d, J = 2.2 Hz; 2H), 4.12 (q, J = 7.2 Hz; 4H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 13.96, 39.05, 40.53, 46.05, 54.17, 60.89, 171.34; IR (nujol) $\nu_{max.}$[cm^{-1}]: 1724 (CO), 1342, 1304 (SO_2), 1259, 1232, 1202, 1163, 1134 (SO_2), 1100, 1016, 907; MS [EI] m/e (%): 316 (1; M^+), 271 (50), 243 (18), 179 (15), 178 (21), 126 (66), 105 (78), 98 (100), 81 (68), 53 (29).

iii. exo-cis-8,9-Bis(hydroxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane 4,4-dioxide (366)

To a stirred suspension of lithium aluminium hydride (0.904g, 23.8 mmol) in dry tetrahydrofuran (50 ml) under nitrogen was added a suspension of dimethyl (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (365; R=Me) (1.860g, 6.46 mmol) in dry tetrahydrofuran (150 ml) over 30 min. The mixture was then stirred and heated under reflux, under a nitrogen atmosphere, for 2h before being cooled to room temperature and the excess of lithium aluminium hydride destroyed by the sequential addition of 10% aqueous tetrahydrofuran (11 ml), 15% sodium hydroxide solution (1.5 ml), and water (20 ml).

Following filtration of the inorganic salts and washing of these with tetrahydrofuran, the combined filtrate and washings were evaporated in vacuo to give a light yellow oil (1.079g). A further quantity of this product (0.483g) was obtained following Soxhlet extraction of the filtered inorganic salts with tetrahydrofuran for 48h. The combined fractions were dried by azeotropic distillation with ethanol, and the residue was triturated using ether with formation of a colourless solid. Filtration of this, followed by drying in vacuo

gave exo-cis-8,9-bis(hydroxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (366) as a finely divided colourless solid (1.090g, 73%), m.p. 122.5-125.5°C.

EA: $C_{10}H_{16}O_4S$ requires 51.7% C, 6.9% H; found 51.5% C, 6.7% H; ^{1}H NMR (CD_3SOCD_3; 80 MHz) δ [ppm]: 2.24 (bd s; 2H), 2.45-2.70 (bd sym m; 2H), 2.83-3.70 (m; 10H), 4.47-4.73 (bd m; 2H); ^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 38.95 (CH), 39.50 (CH), 43.28 (CH), 54.18 (CH_2), 60.36 (CH_2); IR (nujol) $\nu_{max.}$[cm^{-1}]: 3508 and 3446 (OH), 1290 (SO_2), 1244, 1164 (SO_2), 1097, 1019, 988, 700; MS [EI] m/e (%): 233 (0.2; $(M+1)^+$), 184 (1), 149 (4), 131 (4), 119 (23), 105 (28), 91 (46), 84 (100), 83 (80), 79 (45), 67 (92).

iv. (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-Oxa-11-thiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 11,11-dioxide (367)

To a stirred solution of p-toluene sulphonyl chloride (0.605g, 3.18 mmol) in dry pyridine (10 ml) heated under reflux was added, dropwise over a 15 min period, a solution of exo-cis-8,9-bis(hydroxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (366) (0.190g, 0.82 mmol) in dry pyridine (10 ml). After a further 2h, the reaction solution had become dark brown in colour and TLC (silica; 10:90 methylene chloride:ether) analysis indicated the presence of a single component, R_f 0.37. The solution was then cooled, added to crushed ice (50g) and the resultant mixture neutralised by the addition of 10% hydrochloric acid solution. Following extraction with methylene chloride (4 x 50 ml), the combined extracts were washed with water (40 ml), dried over anhydrous magnesium sulphate and the dried filtrate reduced in vacuo to give a dark brown solid. Sublimation of this at 140-150°C, 0.5 mm Hg gave pure colourless crystals of

(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-oxa-11-thiatetracyclo-[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 11,11-dioxide (367) (71 mg, 41%), obtained as long needles, m.p. 169-171°C on recrystallisation from isopropanol.

EA: $C_{10}H_{14}O_3S$ requires 56.0% C, 6.6% H; found 56.1% C, 6.5% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.35 (s; H_2,H_8), 2.89 (d, $J_{3,4a}$ ($J_{6a,7}$) = 3.4 Hz; H_3,H_7), 2.96-3.43 (cm; 6H), 3.56 (dist ddd, $J_{4a,4b}$ ($J_{6a,6b}$) = 9.6 Hz, $J_{3,4a}$ ($J_{6a,7}$) = 3.4 Hz, J = 1.4 Hz; H_{4a},H_{6a}), 3.92 (dist d, $J_{4a,4b}$($J_{6a,6b}$) = 9.6 Hz; H_{4b},H_{6b}); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.51 (CH), 43.41 (CH), 45.00 (CH), 54.60 (CH_2), 73.70 (CH_2); IR (nujol) $\nu_{max.}$[cm^{-1}]: 1298 (SO_2), 1246, 1167 (SO_2), 1106, 1081, 917, 902, 710; MS [CI; NH_3] m/e (%): 232 (100; $(M+NH_4)^+$), 119 (12), 106 (16), 105 (13), 91 (15), 67 (43), 41 (5).

v. [10,10,12,12-$^2H_4$]-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-Oxa-11-thiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 11,11-dioxide (368)

To a solution of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-oxa-11-thiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 11,11-dioxide (367) (68 mg, 0.32 mmol) in dioxan (2 ml) was added 30% sodium deuteroxide in deuterium oxide solution (2.00 ml) and the two layers vigorously stirred and heated under reflux for 6h. On cooling, further dioxan (2 ml) was added and the organic layer separated. The aqueous layer was then extracted with dioxan (2 x 2 ml) and the three organic fractions combined and evaporated in vacuo. Sublimation of the residue at 130°C, 0.01 mm Hg gave [10,10,12,12-$^2H_4$]-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-oxa-11-thiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]-dodecane 11,11-dioxide (368) (53 mg, 77%) as colourless crystals, m.p. 169-170°C.

EA: $C_{10}H_{10}D_4O_3S$ requires 55.0% C, 6.7% (H+D); found 54.8%

C, 6.4% (H+D); ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.35 (s; H_2,H_8), 2.89 (d, $J_{3,4a}(J_{6a,7})$ = 3.4 Hz; H_3,H_7), 3.21 (s; H_1,H_9), 3.56 (dist ddd, $J_{4a,4b}(J_{6a,6b})$ = 9.6 Hz, $J_{3,4a}(J_{6a,7})$ = 3.4 Hz, J = 1.4 Hz; H_{4a},H_{6a}), 3.92 (dist d, $J_{4a,4b}$ ($J_{6a,6b}$) = 9.6 Hz; H_{4b},H_{6b}); ^{2}H NMR ($CHCl_3$; 30.7 MHz) δ [ppm]: 2.97 (bd s; 2D), 3.24 (bd s; 2D); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 2248 (CD), 1287 (SO_2), 1230, 1207, 1178, 1135 (SO_2), 1082, 1039, 994, 851, 807, 691; MS [EI] m/e (%): 219 (1; $(M+1)^+$), 218 (1; M^+), 188 (3), 187 (2), 154 (2), 123 (12), 122 (14), 121 (10), 109 (17), 108 (16), 107 (15), 95 (8), 94 (14), 93 (18), 92 (13), 91 (4), 81 (25), 80 (21), 79 (21), 78 (16), 70 (31), 69 (100), 68 (60).

d. Preparation of 11-benzyl-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thia-11-azatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodecane 5,5-dioxide (370)

i. exo-cis-8,9-Bis(p-toluenesulphonyloxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane 4,4-dioxide (369)

To a stirred solution of p-toluene sulphonyl chloride (2.237g, 11.74 mmol) in pyridine (6 ml) at 0°C was added a solution of exo-cis-8,9-bis(hydroxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane 4,4-dioxide (366) (0.402g, 1.73 mmol) in pyridine (6 ml), dropwise over 30 min. The resultant yellow solution was stirred for a further 3h at 0°C before being poured into iced water (120 ml) with immediate precipitation of a colourless solid.

The mixture was neutralised by addition of 10% hydrochloric acid solution and the solid present removed by filtration, washed well with water and dried in vacuo. This material was twice recrystallised from ethanol to give exo-cis-8,9-bis(p-toluenesulphonyloxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]-

nonane 4,4-dioxide (369) (0.489g, 52%) as colourless crystals, m.p. 142-143°C.

EA: $C_{24}H_{28}O_8S_3$ requires 53.3% C, 5.2% H; found 53.0% C, 5.2% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.40 (s; 2H), 2.45 (s; 6H), 2.65-3.36 (m; 8H), 3.82-4.20 (sym m; 4H), 7.34 and 7.73 (A_2B_2 pattern, J = 8.3 Hz; 8H); ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 21.49 (CH_3), 39.20 (CH), 39.72 (CH), 40.44 (CH), 54.50 (CH_2), 68.73 (CH_2), 127.76 (2xCH), 129.92 (2xCH), 132.71 (Q), 145.08 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1356, 1320, 1192, 1178, 1139, 950, 807, 778, 666; MS [EI] m/e (%): M^+ not apparent, 227 (17), 226 (12), 172 (21), 155 (42), 107 (16), 91 (100), 71 (31), 55 (33); MS [CI; NH_3] m/e(%): $(M+NH_4)^+$ not apparent, 416 (100), 244 (11), 227 (17), 214 (26), 190 (13), 155 (8), 108 (23), 91 (18), 71 (20).

Extraction of the aqueous filtrate and washings using methylene chloride (3 x 100 ml), followed by washing of the combined extracts with water (2 x 75 ml), drying over anhydrous magnesium sulphate and evaporation of the dried filtrate in vacuo gave a colourless solid. Recrystallisation of this from methylene chloride/diisopropyl ether, and then from isopropanol gave (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-oxa-11-thiatetracyclo[7.3.0.0^{2,8}.0^{3,7}]-dodecane 11,11-dioxide (367) (20 mg, 5%) as colourless crystals, m.p. 168-171°C, displaying identical ^{1}H and ^{13}C NMR spectra to those of an authentic sample (see p.515).

ii. 11-Benzyl-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thia-11-azatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodecane 5,5-dioxide (370)

A mixture of exo-cis-8,9-bis(p-toluenesulphonyloxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]nonane 4,4-dioxide

(369) (0.589g, 1.09 mmol) and benzylamine (0.349g, 3.26 mmol) in ethanol (15 ml) was stirred and heated under reflux for 54h, by which time TLC (alumina; ether) indicated the absence of starting material (369) and the presence of a single product, R_f 0.45. On cooling, the reaction solution was evaporated to dryness *in vacuo* and triturated with methylene chloride. The insoluble *p*-toluene sulphonic acid present was removed by filtration, and the filtrate was evaporated *in vacuo* to give a residue of light yellow oil. Trituration with *n*-hexane gave a colourless solid which was filtered off and recrystallised from ethanol to yield 11-benzyl-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thia-11-azatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 5,5-dioxide (370) (0.193g, 58%) as colourless crystals, m.p. 121.5-123.5°C.

EA: $C_{17}H_{21}NO_2S$ requires 67.3% C, 7.0% H, 4.6% N; found 67.1% C, 6.9% H, 4.9% N; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.18 (dd, J = 9.4 Hz, 5.3 Hz; 2H), 2.36 (s; 2H), 2.64-3.20 (cm; 10H), 3.60 (s; 2H), 7.28 (bd s; 5H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.61 (2xCH), 43.85 (2xCH), 44.41 (2xCH), 54.72 (2xCH_2), 59.50 (CH_2), 59.66 (2xCH_2), 126.56 (CH), 127.92 (2xCH), 128.34 (2xCH), 139.19 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1376, 1346, 1305 (SO_2), 1250, 1167, 1137 (SO_2), 1105, 842, 739, 702; MS [EI] m/e (%): 303 (55; M^+), 302 (19), 226 (13), 212 (44), 133 (12), 120 (15), 92 (32), 91 (100), 67 (29), 42 (52).

e. Preparation of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5,11-dithiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 5,5-dioxide (371)

To a solution of sodium sulphide nonahydrate (0.559g, 2.33 mmol) in 50% aqueous ethanol (20 ml) was added exo-cis-8,9-bis(*p*-toluenesulphonyloxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (369) (0.416g, 0.77 mmol) and the resultant mixture heated under reflux for 5h. On cooling, the reaction

mixture was evaporated to dryness *in vacuo* and dissolved in water (50 ml) and methylene chloride (40 ml). The organic layer was separated and the aqueous layer extracted with methylene chloride (2x40 ml). Drying of the combined organic fractions over anhydrous magnesium sulphate and evaporation of the dried filtrate gave, on recrystallisation of the residue from isopropanol, (*cis*-1-*transoid*-1,2-*cis*-2-*transoid*-2,3-*cis*-3)-5,11-dithiatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodecane 5,5-dioxide (371) (0.109g, 62%) as a colourless powder, m.p. 136-139°C.

EA: $C_{10}H_{14}O_2S_2$ requires 52.1% C, 6.1% H; found 52.0% C, 5.9% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.24 (s; 2H), 2.69-3.42 (cm; 12H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.43 (CH), 38.83 (CH_2), 43.40 (CH), 48.11 (CH), 54.61 (CH_2); IR (nujol) $\nu_{max.}$[cm^{-1}]: 1312 (SO_2), 1254, 1194, 1139, 1124 (SO_2), 1094, 897, 838, 709; MS [EI] m/e (%): 230 (17; M^+), 196 (2), 164 (2), 119 (8), 117 (4), 105 (8), 99 (100), 91 (12), 67 (44).

f. Preparation of (*cis*-1-*transoid*-1,2-*cis*-2-*transoid*-2,3-*cis*-3)-5,11-dithiatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodecane 5,5,11,11-tetraoxide (372)

A solution of (*cis*-1-*transoid*-1,2-*cis*-2-*transoid*-2,3-*cis*-3)-5,11-dithiatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodecane 5,5-dioxide (371) (85 mg, 0.370 mmol) in dry methylene chloride (3 ml) was stirred at 0°C during the dropwise addition, over a 30 min period, of a solution of *m*-chloroperoxybenzoic acid (158 mg '85%', 0.779 mmol) in dry methylene chloride (10 ml). After stirring at room temperature for 140h, the resultant solution was evaporated to dryness and the colourless solid obtained washed well with 80% saturated sodium carbonate solution, then with water, and dried *in vacuo*. Sublimation of this material at 220°C, 6 x 10^{-3} mm Hg gave (*cis*-1-*transoid*-1,2-

cis-2-transoid-2,3-cis-3)-5,11-dithiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$] dodecane 5,5,11,11-tetraoxide (372) (63 mg, 65%) as a colourless solid, m.p. 284-288°C (lit.[112] m.p. 288°C).

EA: $C_{10}H_{14}O_4S_2$ requires 45.8% C, 5.4% H; found 46.0% C, 5.3% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.73 (bd s; 2H), 2.96-3.31 (cm; 12H); ^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 38.49 (2xCH), 42.92 (CH), 53.87 (2xCH_2); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1302 (SO_2), 1252, 1213, 1163, 1144, 1131 (SO_2), 1106, 904, 726; MS [EI] m/e (%): M^+ not apparent, 198 (2; $(M-SO_2)^+$), 183 (3), 133 (17), 119 (44), 117 (21), 106 (28), 105 (41), 93 (58), 92 (56), 91 (97), 79 (91), 77 (82), 67 (100).

3. Preparation of miscellaneous systems containing a 4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane 4,4-dioxide skeleton

a. Preparation of 8,9-dimethylene-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0]nonane 4,4-dioxide (374)

i. exo-cis-8,9-Bis(iodomethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (373)

A mixture of exo-cis-8,9-bis(p-toluenesulphonyloxymethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (369) (2.139g, 3.96 mmol) and sodium iodide (1.783g, 11.9 mmol) in ethyl methyl ketone (25 ml) was stirred and heated under reflux for 42h. The resultant mixture was cooled and evaporated to dryness in vacuo, after which the residue was dissolved in water (20 ml) and methylene chloride (20 ml). After separating the organic layer, the aqueous fraction was extracted with methylene chloride (2x15 ml) and the organic fractions combined, washed with saturated sodium thiosulphate solution (20 ml) and dried over anhydrous magnesium sulphate. Evaporation of the dried filtrate gave a brown oil which comprised of four components as indicated by TLC (silica; ether): R_f 0.21, 0.40 (major), 0.65 and 0.75.

Flash chromatography (silica; 50:50 ⟶ 75:25 ether:pet-ether (b.p. 40-60°C)) of the crude product mixture allowed separation of the major component [TLC (silica; ether) R_f 0.40] identified as exo-cis-8,9-bis(iodomethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (373) (0.371g, 21%) as colourless crystals, m.p. 150-152.5°C, on recrystallisation from methylene chloride/diisopropyl ether.

EA: $C_{10}H_{14}I_2O_2S$ requires 26.6% C, 3.1% H; found 26.6% C, 3.0% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.38 (s; 2H), 2.79-3.57 (m; 12H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 4.86, 39.01, 43.57, 46.50, 54.59; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1297 (SO_2), 1254, 1235, 1190, 1153, 1134 (SO_2), 1108, 1089, 895, 738; MS [EI] m/e (%): 452 (0.4; M^+), 451 (0.4), 325 (3), 258 (16), 207 (3), 198 (35), 181 (4), 167 (4), 133 (22), 132 (8), 131 (23), 105 (11), 91 (21), 80 (10), 79 (8), 77 (6), 67 (100), 41 (10).

ii. 8,9-Dimethylene-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0]nonane 4,4-dioxide (374)

To a stirred mixture of exo-cis-8,9-bis(iodomethyl)-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (373) (0.371g, 0.82 mmol) in dry tetrahydrofuran (15 ml) at room temperature was added a dispersion of sodium hydride (0.146g '60%', 3.65 mmol) in mineral oil. The course of the reaction was followed by TLC (silica; ether) which indicated the increasing formation of a product spot, R_f 0.52, at the expense of starting material (373). For completion of reaction, further portions of sodium hydride in mineral oil were added after 70h (0.222g '60%', 5.55 mmol) and 90h (0.424g

'60%', 10.60 mmol), with TLC analysis indicating the absence of (373) some 25h after the final addition.

Water (15 ml) was carefully added to the reaction mixture to destroy the excess of sodium hydride, and the mixture was reduced in vacuo (at room temperature) to small volume (15 ml), extracted with methylene chloride (4x15 ml) and the combined extracts dried over anhydrous magnesium sulphate. Evaporation of the dried filtrate and trituration of the residue with n-hexane followed by filtration and drying in vacuo (at room temperature) of the filtered solid gave 8,9-dimethylene-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0]nonane 4,4-dioxide (374) (0.137g, 85%) as a colourless powder, m.p. 95-98°C, on recrystallisation from methylene chloride/diisopropyl ether.

EA: $C_{10}H_{12}O_2S$ requires 61.2% C, 6.2% H; found 60.9% C, 6.2% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.02-3.35 (m; 8H), 4.82 (s; 2H), 5.23 (s; 2H); ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.99 (CH), 46.41 (CH), 54.60 (CH_2), 105.17 (CH_2), 150.80 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1297 (SO_2), 1246, 1212, 1139 (SO_2), 1103, 962, 896, 724; MS [EI] m/e (%): 196 (5; M^+), 132 (18), 131 (49), 117 (100), 104 (34), 91 (67), 79 (12), 78 (16), 77 (15), 64 (24).

b. Preparation and reactivity of 8-bromo-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (375)

i. Preparation of 8-bromo-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (375)

To a stirred solution of exo-8-endo-9-dibromo-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (309) (0.185g, 0.561 mmol) in dry tetrahydrofuran (10 ml) under nitrogen was added

freshly sublimed potassium t-butoxide (69 mg, 0.616 mmol) and the resultant mixture stirred at room temperature for 5h. TLC (silica; ether) analysis after this time indicated the absence of starting dibromide (309), R_f 0.50, and presence of a single product spot, R_f 0.40. Addition of water (0.5 ml) destroyed the excess of potassium t-butoxide, and the reaction mixture was then evaporated to dryness under reduced pressure. The residue was dissolved in methylene chloride (15 ml) and water (15 ml), the organic layer separated and the aqueous layer extracted with methylene chloride (3x15 ml). Combination of the organic fractions and washing with water (10 ml) followed by drying over anhydrous magnesium sulphate gave, on evaporation of the dried filtrate, a residue of colourless solid (0.138g). Recrystallisation from methylene chloride/diisopropyl ether gave 8-bromo-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-non-8-ene 4,4-dioxide (375) (0.121g, 87%) as colourless flakes, m.p. 131-132°C.

EA: $C_8H_9BrO_2S$ requires 38.6% C, 3.6% H; found 38.3% C, 3.4% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.79-3.02 (m; 2H), 3.04-3.51 (m; 6H), 6.38 (dd, J = 1.8Hz; 0.7 Hz; 1H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 33.59, 35.63, 46.61, 53.38, 53.51, 54.11, 122.46 (Q), 140.04; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1562 (C=C), 1320, 1294 (SO_2), 1229, 1141 (SO_2), 894, 873, 853, 802, 706, 695; MS [EI] m/e (%): 250 (2; $^{81}M^+$), 248 (2; $^{79}M^+$), 185 (8), 184 (12), 183 (9), 182 (12), 171 (55), 169 (53), 158 (22), 156 (22), 132 (8), 130 (8), 105 (100).

ii. Reactivity of 8-bromo-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (375)

α. Dehydrobromination: attempted preparation of 1,11-diphenyl-(cis-3-transoid-3,4-cis-4)-12,13-benzo-14-oxa-6-thiapentacyclo-[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]tetradeca-2(10),12-diene 6,6-dioxide (377)

A solution of 8-bromo-(cis-1-transoid-1,2-cis-2)-4-thia-tricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (375) (62 mg, 0.25 mmol) and 1,3-diphenylisobenzofuran (292) (0.132g, 0.49 mmol) in dry tetrahydrofuran (5 ml) was stirred at -78°C under nitrogen during the addition of a solution of lithium bis(trimethylsilyl)amide in tetrahydrofuran (0.37 ml 1.0M solution, 0.37 mmol), via syringe, over a 30 min period. The reaction solution was stirred at -78°C for 3.5h and then allowed to warm to room temperature (with development of a red colouration), and then stirred under nitrogen for a further 18h.

The excess of base was destroyed by careful addition of water (15 ml) and the resultant mixture extracted with methylene chloride (4x8 ml), the extracts combined, washed with water (15 ml) and dried over anhydrous magnesium sulphate. On evaporation of the dried filtrate, a viscous yellow oil (0.170g) was obtained which was found on TLC (silica; ether) analysis to consist of four components, R_f 0.77, 0.68, 0.53 and 0.40. Separation by MPLC (silica; pet-ether (b.p. 40-60°C)→ether) gave unidentified, purely aromatic, compounds for the components at R_f 0.77 and 0.68, and recovered starting olefin (375) (13 mg, 21%) (R_f 0.40). The component at R_f 0.53 was identified as 2-bromo-cis-1,11-diphenyl-(cis-3-transoid-3,4-cis-4)-12,13-benzo-14-oxa-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]tetradec-12-ene 6,6-dioxide (378) (48 mg, 37%), obtained as colourless crystals, m.p. (decomp.) 172-175°C.

EA: $C_{28}H_{23}BrO_3S$ requires 64.7% C, 4.5% H; found 64.5% C, 4.7% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.45 (d, J = 4.7 Hz; 1H), 2.73 (dd, J = 4.7Hz; 1.8 Hz; 1H), 2.89-2.99 (m; 2H), 3.08 (s; 1H), 3.11-3.30 (m; 3H), 3.71-3.83 (bd sym m; 1H), 7.00-7.04 (m; 1H), 7.20-7.25 (m; 2H), 7.28-7.35 (m; 2H), 7.39-7.53 (m; 7H), 7.90-7.95 (m; 2H); ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 36.81 (CH), 38.02 (CH), 38.35 (CH), 44.41 (CH), 54.50 (CH_2), 54.55 (CH_2), 60.52 (CH), 69.76 (Q), 89.91 (Q), 91.97 (Q), 119.31 (CH), 122.08 (CH), 126.18 (2xCH), 126.87 (CH), 127.34 (2xCH), 127.51 (CH), 128.12 (CH), 128.28 (3xCH), 128.65 (2xCH), 133.74 (Q), 135.22 (Q), 145.43 (Q), 146.06 (Q); IR (nujol) $\nu_{max.}$[cm^{-1}]: 1345, 1304 (SO_2), 1254, 1236, 1179, 1137 (SO_2), 1098, 980, 904, 856, 755, 734, 699, 664; MS [EI] m/e (%): 519 (1; $(^{81}M-H)^+$), 517 (1; $(^{79}M-H)^+$), 439 (5), 421 (4), 420 (10), 374 (2), 356 (21), 270 (25), 105 (49), 82 (100), 81 (45), 80 (99), 79 (44).

β. Diels-Alder reactions

β1. With 1,3-diphenylisobenzofuran (292)

A solution of 8-bromo-(cis-1-transoid-1,2-cis-2)-4-thia-tricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (375) (47 mg, 0.19 mmol) and 1,3-diphenylisobenzofuran (292) (56 mg, 0.21 mmol) in dry tetrahydrofuran (5 ml) was stirred at room temperature in the absence of light for 21h, by which time the green/yellow colour associated with the diene had disappeared. TLC (silica; ether) indicated that a large quantity of unreacted olefin (375) (R_f 0.40) was present, together with a minor amount of a product, R_f 0.53, and diene (292) by-products, R_f 0.77 and 0.68. Further 1,3-diphenylisobenzofuran (292) (56 mg, 0.21 mmol) was added and the solution heated under reflux for 6h. Evaporation of the cooled reaction solution followed by preparative

TLC (silica; ether) of the residue gave, as the only two sulphone-containing compounds present, recovered olefin (375) (28 mg, 60% recovered) [R_f 0.40] and 2-bromo-cis-1,11-diphenyl-(cis-3-transoid-3,4-cis-4)-12,13-benzo-14-oxa-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]-tetradec-12-ene 6,6-dioxide (378) (28 mg, 29%) [R_f 0.53], identical in all respects to that described earlier (p.525).

β2. With tetraphenylcyclopentadienone (294)

A solution of 8-bromo-(cis-1-transoid-1,2-cis-2)-4-thia-tricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (375) (91 mg, 0.36 mmol) and tetraphenylcyclopentadienone (294) (0.140 g, 0.36 mmol) in dry benzene (10 ml) was heated under reflux for 95h. TLC (silica; ether) analysis of the purple solution confirmed the presence of both starting materials and demonstrated a single product spot at R_f 0.45. Continued heating under reflux of the solution for an additional 30h resulted in no significant change in the relative quantities of the three components as indicated by TLC, and therefore the reaction solution was cooled and evaporated in vacuo. Trituration of the resultant viscous oil with ether gave a slightly purple solid (0.101 g) which was filtered off and dried: TLC (silica; ether) analysis indicated this to comprise a single component, R_f 0.45. Evaporation of the trituration filtrate followed by preparative TLC (silica; ether) of the residue allowed separation of starting olefin (375) (20 mg; 22%) [R_f 0.40], and of further of the above product (35 mg) [R_f 0.45]. Recrystallisation of the combined crops of product from methylene chloride/diisopropyl ether gave 2-bromo-14-oxo-1,11,12,13-tetraphenyl-(cis-3-transoid-3,4-cis-4)-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]tetradec-12-ene 6,6-dioxide (379) (82 mg, 35%) as a light purple solid, m.p. (decomp.) 177-179°C.

EA: $C_{37}H_{29}BrO_3S$ requires 70.1% C, 4.6% H; found 70.2% C, 4.7% H; ^{1}H NMR (CD_3COCD_3; 80 MHz) δ [ppm]: 2.30-2.42 (bd sym m; 1H), 2.78 (s; 1H), 2.92-3.18 (m; 2H), 3.22-3.40 (m; 2H), 3.45-3.72 (m; 1H), 3.81 (d, J = 2 Hz; 1H), 4.12 (tt, J = 8 Hz, 2 Hz; 1H), 6.85-7.41 (cm; 20H); ^{13}C NMR (CD_3COCD_3; 50.3 MHz) δ [ppm]: 35.51, 36.48, 37.80, 44.16, 53.16, 53.25, 55.30, 66.45 (Q), 69.85 (Q), 71.57 (Q), 126.18 (3xCH), 126.37, 126.50, 126.71, 126.86 (2xCH), 127.09 (2xCH), 127.20 (Q), 127.42 (2xCH), 129.06 (2xCH), 129.25 (2xCH), 129.90 (2xCH), 130.47 (2xCH), 131.33 (Q), 132.89 (Q), 134.00 (Q), 143.02 (Q), 143.32 (Q), 194.83 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1786 (CO), 1496, 1299 (SO_2), 1172, 1134 (SO_2), 1098, 1071, 1026, 730, 695; MS [EI] m/e (%): M^+ not apparent, 462 (39), 460 (100), 432 (5), 383 (4), 352 (4), 282 (11), 206 (6), 177 (12), 91 (6), 78 (7).

iii. Attempted preparation of 14-oxo-1,11,12,13-tetraphenyl-(cis-3-transoid-3,4-cis-4)-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]-tetradeca-2(10),12-diene 6,6-dioxide (380)

α. Using 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU)

A solution of 2-bromo-14-oxo-1,11,12,13-tetraphenyl-(cis-3-transoid-3,4-cis-4)-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]tetradec-12-ene 6,6-dioxide (379) (29 mg, 0.046 mmol) in dry tetrahydrofuran (1.5 ml) was stirred at 0°C under nitrogen during the addition of a solution of 1,8-diazobicyclo[5.4.0]undec-7-ene (18 mg, 0.12 mmol) in dry tetrahydrofuran (1.5 ml), via syringe, over a 20 min period. The resultant solution was stirred at 45°C and monitored at regular intervals using TLC (silica; ether), which indicated only the presence of starting material (379) (R_f 0.45) on heating for 70h.

After this time, the solution was cooled and evaporated to dryness in vacuo. The residue was dissolved in methylene chloride

(20 ml) and washed in turn with 0.1M hydrochloric acid solution (10 ml), saturated sodium chloride solution (10 ml) and finally water (10 ml) before being dried over anhydrous magnesium sulphate. Evaporation of the dried filtrate gave a light yellow solid (37 mg), found to contain recovered starting sulphone (379) in quantitative yield by ^{1}H NMR analysis.

β. Using potassium t-butoxide

To a solution of 2-bromo-14-oxo-1,11,12,13-tetraphenyl-(cis-3-transoid-3,4-cis-4)-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]-tetradec-12-ene 6,6-dioxide (379) (29 mg, 0.046 mmol) in dry tetrahydrofuran (1 ml), stirred at room temperature under nitrogen, was added powdered potassium t-butoxide (22 mg, 0.15 mmol) with an immediate darkening of the colour of the reaction mixture. TLC (silica; ether) analysis after stirring for 1h indicated the presence of starting sulphone (379) (R_f 0.45) only. As no change in the TLC profile was observed after a further 17h, further potassium t-butoxide (38 mg, 0.25 mmol) was added; after 2h, TLC analysis indicated the absence of starting sulphone (379).

Following the addition of 20% aqueous tetrahydrofuran (1 ml), the resultant mixture was evaporated to dryness and the residue dissolved in water (10 ml) and methylene chloride (10 ml). The organic layer was separated and the aqueous layer extracted with methylene chloride (3x10ml), the organic fractions combined, dried over anhydrous magnesium sulphate and the dried filtrate evaporated under reduced pressure to give a residue of orange solid (10 mg). TLC (silica; ether) analysis of this gave only a baseline streak; ^{1}H NMR analysis indicated the absence of sulphone-containing compounds.

F. Flash Vacuum Pyrolysis (FVP) of Systems Containing a transoid-4-Thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide Skeleton

1. FVP of tricyclic systems containing a transoid-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane 4,4-dioxide skeleton

a. FVP of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane 4,4-dioxide (307) and related systems

i. (cis-1-transoid-1,2-cis-2)-4-Thiatricyclo[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (307)

FVP [60°C, 650°C, 10^{-2} mm Hg] of the title compound (307) (15 mg, 8.7 x 10^{-2} mmol) gave a mixture of a yellow oil and a colourless polymeric solid. After addition of deuteriochloroform (0.6 ml), the polymer was removed by filtration. TLC (silica; ether) analysis of the pyrolysate indicated the absence of (307) or sulphone-containing products; GLC (10% PEGA; 90°C) and ^{1}H NMR analyses indicated, on comparison of retention times and ^{1}H NMR spectra with those of authentic samples, the presence of 4-vinylcyclohex-1-ene (42% yield), cycloocta-(Z,Z)-1,5-diene (17%) and buta-1,3-diene (not quantified) [yields estimated from ^{1}H NMR spectra by addition of chloroform (7.0 mg)].

ii. (cis-1-transoid-1,2-cis-2)-4,9-dithiatricyclo[5.3.0.$0^{2,6}$]-decane 4,4,9,9-tetraoxide (390)

The pyrolysis conditions described by Buchan[29] were used. FVP [300°C, 650°C, 10^{-2} mm Hg] of the title compound (390) (82.5 mg, 0.35 mmol) gave a light yellow oil which was found to be completely soluble in ether. Analysis of this solution by GLC (10% PEGA; 90°C) and comparison of retention times and peak areas with those of standard solutions allowed identification of the products as 4-vinylcyclohex-1-

ene (32% yield), cycloocta-(Z,Z)-1,5-diene (4%) and buta-1,3-diene (not quantified).

b. FVP of dimethyl (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (365; R = Me) and related systems

i. Dimethyl (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylate 4,4-dioxide (365; R = Me)

FVP [210-220°C, 650°C, 2 x 10^{-3} mm Hg] of the title compound (365; R = Me) (27.0 mg, 9.4 x 10^{-2} mmol) gave a colourless oil which was dissolved in deuteriochloroform. Analysis of this solution by ^{1}H and ^{13}C NMR spectroscopy (followed by addition of methylene chloride to permit assessment of yields), and by GLC (10% PEGA; 130°C) and GC-MS indicated the presence of (Z)- and (E)-isomers of methyl penta-2,4-dienoate, respectively (397) (16% yield) and (396) (77% yield). Separation of the isomers was achieved by preparative GLC (10% PEGA; 85°C) to give, in order of increasing t_R:

(a) methyl (Z)-penta-2,4-dienoate (397):- ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 3.71 (s; 3H), 5.51 (d, $J_{4,5a}$ = 10.5 Hz; H_{5a}), 5.52 (d, $J_{4,5b}$ = 16.0 Hz; H_{5b}), 5.68 (d, $J_{2,3}$ = 10.5 Hz; H_2), 6.55 (t, $J_{2,3}$ = $J_{3,4}$ = 10.5 Hz; H_3), 7.58 (dt, $J_{4,5b}$ = 16.0 Hz, $J_{3,4}$ = $J_{4,5a}$ = 10.5 Hz; H_4); MS [GC-MS] m/e (%): 113 (5; $(M+1)^+$), 112 (71; M^+), 111 (32), 97 (22), 82 (23), 81 (96), 69 (8), 54 (7), 53 (100), 52 (11), 51 (13).

(b) methyl (E)-penta-2,4-dienoate (396):- ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 3.74 (s; 3H), 5.48 (ddd, $J_{4,5a}$ = 10.0 Hz, $J_{5a,5b}$ = 1.4 Hz, $J_{3,5a}$ = 0.7 Hz; H_{5a}), 5.60 (ddd, $J_{4,5b}$ = 16.9 Hz, $J_{5a,5b}$ = 1.4 Hz, $J_{3,5b}$ = 0.7 Hz; H_{5b}), 5.91 (dd, $J_{2,3}$ = 15.5 Hz, $J_{2,4}$ = 0.7 Hz; H_2),

6.45 (dddd, $J_{4,5b}$ = 16.9 Hz, $J_{3,4}$ = 10.9 Hz, $J_{4,5a}$ = 10.0 Hz, $J_{2,4}$ = 0.7 Hz; H_4), 7.26 (ddt, $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 10.9 Hz, $J_{3,5a}$ = $J_{3,5b}$ = 0.7 Hz; H_3) [similar to lit.[234] ^{1}H NMR spectrum]; ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 51.34, 121.58, 125.38, 134.55, 144.68, 167.03; IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2954 (CH), 1723 (CO), 1646 (C=C), 1602 (C=C), 1435, 1312, 1271, 1207, 1147, 1011, 868; MS [GC-MS] m/e (%): 113 (4; $(M+1)^+$), 112 (54; M^+), 97 (12), 82 (16), 81 (100), 69 (4), 59 (4), 54 (5), 53 (79), 52 (8), 51 (9).

ii. Dimethyl trans/cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylates (394)/(395) and dimethyl cycloocta-(Z,Z)-3,7-diene-cis-1,2-dicarboxylate (392)

FVP [100-120°C, 650°C, 6 x 10^{-3} mm Hg] of a 70:25:5 mixture of the title compounds (394), (395) and (392) (10.7 mg, 4.8 x 10^{-2} mmol) gave a yellow liquid which was dissolved, whilst still cold, in deuteriochloroform. Analysis of the product solution by ^{1}H NMR and GLC (10% PEGA; 130°C) and comparison against authentic samples obtained by an independent route indicated the presence of (Z)- and (E)-isomers of methyl penta-2,4-dienoate, respectively (397) (13% yield) and (396) (66% yield).

c. FVP of 8,9-dimethylene-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane 4,4-dioxide (374)

FVP [80°C, 600°C, 4 x 10^{-3} mm Hg] of the title compound (3 mg volatilised, 1.5 x 10^{-2} mmol; 18 mg polymerised in inlet on heating) gave a yellow liquid and a colourless polymeric solid. The former was dissolved in deuteriochloroform and analysed by ^{1}H NMR spectroscopy and by GLC (5% SE 30; 100°C) and GC-MS. Starting diene (374) was found to be absent - four volatile components were detected and

quantified (in order of increasing t_R): $C_{10}H_{12}$ (41% yield), $C_{10}H_{12}$ (8%), $C_{10}H_{12}$ (8%) and $C_{10}H_{10}$ (2%). The major product was tentatively assigned to 3,4-dimethylene-5-vinylcyclohex-1-ene (409): ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.70-2.14 (m; 3H), 4.82 (bd s; 2H), 4.95-5.24 (cm; 2H), 5.32 (bd s; 2H), 5.81-6.30 (cm; 3H); MS[GC-MS] m/e (%): 132 (59; M^+), 131 (18), 117 (100), 116 (18), 115 (47), 91 (32), 77 (11), 65 (13), 63 (10), 51 (12), 39 (14).

d. FVP of transoid (208) and cisoid (209) isomers of 4-thiatricyclo-[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide

i. (cis-1-transoid-1,2-cis-2)-4-Thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (208)

α. At 400°C

FVP [65°C, 400°C, 6 x 10^{-3} mm Hg] of the title compound (208) (21 mg, 12.4 x 10^{-2} mmol) gave a colourless oil (20 mg) which was dissolved in deuteriochloroform whilst still cold. Analysis of the pyrolysate solution by ^{1}H NMR spectroscopy established the presence of starting olefin (208) (22% recovered) and cis-8-thiabicyclo[4.3.0]-nona-2,4-diene 8,8-dioxide (212) (73% yield) [identified by comparison of the ^{1}H NMR spectrum with that of an authentic sample].

β. At 650°C

FVP [95-100°C, 650°C, 5 x 10^{-3} mm Hg] of the title compound (208) (22.3 mg, 13.1 x 10^{-2} mmol) gave a light yellow oil found from ^{1}H NMR spectroscopy to be purely cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (15.7 mg, 70%).

ii. (cis-1-cisoid-1,2-cis-2)-4-Thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (209)

FVP [60°C, 400°C, 2.5 x 10^{-3} mm Hg] of the title compound (209) (4 mg, 2.4 x 10^{-2} mmol) gave a colourless liquid (4 mg) which was dissolved in deuteriochloroform whilst still cold. ^{1}H NMR spectroscopic analysis indicated this to consist of a mixture of starting olefin (209) (est. 6%) and cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (est. 94% yield).

2. FVP of transoid,transoid-10-hetero-5-thiatetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane 5,5-dioxide systems (278)

a. FVP of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-10-oxa-5-thiatetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane 5,5-dioxide (278; X = O) and derived systems

i. (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-10-Oxa-5-thiatetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane 5,5-dioxide (278; X = O)

α. At 500°C

FVP [130°C, 500°C, 10^{-2} mm Hg] of the title compound (278; X = O) (89 mg, 0.48 mmol) gave a light yellow oil (62 mg). TLC (silica; ether) analysis indicated the presence of two major components at R_f 0.38 and 0.50, and two minor components at R_f 0.70 and 0.75. Separation of the two most abundant components was achieved by preparative TLC (silica; ether) giving:

(i) R_f 0.50, a colourless, crystalline solid identified as trans-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (418; X = O) (13 mg, 15%), obtained as fine needles, m.p. 125-126°C, on recrystallisation from methylene chloride/diisopropyl ether.

EA: $C_8H_{10}O_3S$ requires 51.6% C, 5.4% H; found 51.5% C, 5.4% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.92 (dist t, $J_{1,10a}$ ($J_{7,8a}$) = $J_{10a,10b}$ ($J_{8a,8b}$) = 12.4 Hz; H_{8a}, H_{10a}), 3.15-3.25 (sym m; H_1,H_7), 3.52 (dd, $J_{10a,10b}$ ($J_{8a,8b}$) = 12.4 Hz, $J_{1,10b}$ ($J_{7,8b}$) = 6.5 Hz; H_{8b}, H_{10b}), 4.70 (dd, $J_{2,3}$ ($J_{5,6}$) = 7.4 Hz, $J_{1,2}$ ($J_{6,7}$) = 1.9 Hz; H_2, H_6), 6.23 (dd, $J_{2,3}$ ($J_{5,6}$) = 7.4 Hz, $J_{1,3}$ ($J_{5,7}$) = 2.2 Hz; H_3, H_5); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 40.56 (CH), 58.85 (CH_2), 106.07 (CH), 142.97 (CH); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1660, 1642, 1351, 1305 (SO_2), 1290, 1238, 1202, 1128 (SO_2), 996, 902, 812, 754; MS [EI] m/e (%): 186 (60; M^+), 121 (100), 120 (58), 103 (56), 93 (37), 91 (42), 79 (44), 77 (30), 68 (63), 53 (61).

(ii) R_f 0.38, a colourless, crystalline solid identified as cis-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = O) (25 mg, 28%), m.p. 78-78.5°C on recrystallisation from methylene chloride/diisopropyl ether.

EA: $C_8H_{10}O_3S$ requires 51.6% C, 5.4% H; found 51.6% C, 5.3% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 3.01-3.12 (m; 2H), 3.21-3.44 (cm; 4H), 4.76 (dd, $J_{2,3}$ ($J_{5,6}$) = 7.8 Hz, $J_{1,2}$ ($J_{6,7}$) = 5.1 Hz; H_2, H_6), 6.27 (dd, $J_{2,3}$ ($J_{5,6}$) = 7.8 Hz, $J_{1,3}$ ($J_{5,7}$) = 0.9 Hz; H_3, H_5); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 39.38 (CH), 58.84 (CH_2), 105.52 (CH), 143.67 (CH); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1667, 1652, 1337, 1314 (SO_2), 1288, 1269, 1230, 1214, 1168, 1132, 1111 (SO_2), 744; MS [EI] m/e (%): 186 (100; M^+), 121 (56), 103 (29), 93 (43), 91 (38), 81 (51), 79 (56), 77 (78), 68 (68), 66 (71), 53 (70).

β. At 400°C

FVP [120°C, 400°C, 6 x 10^{-3} mm Hg] of the title compound (278; X = O) (25 mg, 0.13 mmol) gave a mixture of a colourless solid

and liquid. This was dissolved in deuteriochloroform whilst still cold and found on analysis by ^{1}H NMR spectroscopy to consist of starting epoxide (278; X = 0) (est. 60% recovery), cis-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = 0) (est. 27% yield) and trans-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (418; X = 0) (est. 13%).

γ. At 650°C

FVP [150°C, 650°C, 8 x 10^{-3} mm Hg] of the title compound (278; X = 0) (27.8 mg, 0.149 mmol) gave a pyrolysate of a yellow oil and colourless polymeric solid. While still cold, the oil was dissolved in deuteriochloroform; analysis by ^{1}H NMR spectroscopy indicated the presence of cis-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = 0) (est. 22% yield), toluene (13%) and benzene (6%).

δ. At 750°C

FVP [150°C, 750°C, 4 x 10^{-3} mm Hg] of the title compound (278; X = 0) (10 mg, 5.4 x 10^{-2} mmol) gave a yellow oil. This was dissolved in deuteriochloroform (whilst still cold) and analysed by ^{1}H NMR spectroscopy (yields calculated by addition of a measured quantity of methylene chloride) and GLC (10% PEGA; 90°C): benzene (19% yield) and toluene (21%) were found to be present.

ii. FVP of cis-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = 0)

FVP [110°C, 500°C, 6 x 10^{-3} mm Hg] of the title compound (416; X = 0) (4 mg, 2 x 10^{-2} mmol) gave a colourless solid, found by ^{1}H NMR spectroscopy to be purely starting sulphone (416; X = 0) (4 mg, quantitative recovery).

iii. FVP of trans-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (418; X = 0)

FVP [110°C, 500°C, 6 x 10^{-3} mm Hg] of the title compound (418; X = 0) (2 mg, 1 x 10^{-2} mmol) gave a colourless solid. Analysis of this by ^{1}H NMR spectroscopy indicated the presence of pure starting sulphone (418; X = 0), recovered quantitatively.

iv. FVP of cis/trans-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = 0)/(418; X = 0)

FVP [135°C, 750°C, 5 x 10^{-3} mm Hg] of a 2:1 mixture of the title compounds (416; X = 0) and (418; X = 0) (11 mg, 5.9 x 10^{-2} mmol) gave a mixture of colourless liquid and colourless polymeric solid. The liquid product was dissolved in deuteriochloroform and analysed by ^{1}H NMR spectroscopy. Benzene (13% yield) and toluene (21%) were identified.

v. Hydrogenation of cis- and trans-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = 0), (418; X = 0)

α. Preparation of cis-4-oxa-9-thiabicyclo[5.3.0]decane 9,9-dioxide (419; X = 0)

To a solution of cis-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = 0) (18 mg, 9.7 x 10^{-2} mmol) in methanol (15 ml) was added 10% palladium-on-charcoal (14 mg) and the mixture hydrogenated at one atmosphere pressure of hydrogen for 2h. TLC (silica; ether) analysis indicated the absence of starting sulphone (416; X = 0) (R_f 0.38) and the presence of a single product, R_f 0.07. Thus, the catalyst was filtered off, washed with further methanol and the combined filtrate and washings evaporated in vacuo to give cis-4-oxa-9-thiabicyclo[5.3.0]-

decane 9,9-dioxide (419; X = 0) (16 mg, 87%) as a colourless oil which could not be induced to crystallise.

EA: $C_8H_{14}O_3S$ requires 50.5% C, 7.4% H; found 50.4% C, 7.6% H; ^1H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.77-2.06 (m; 4H), 2.70-3.65 (cm; 8H), 3.75-4.07 (m; 2H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 33.25 (CH_2), 37.42 (CH), 56.32 (CH_2), 68.18 (CH_2); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2940 (CH), 2848 (CH), 1443, 1411, 1297 (SO_2), 1244, 1205, 1120 (SO_2), 1057, 1013, 846, 812; MS [EI] m/e (%): 191 (5; $(M+1)^+$), 190 (5; M^+), 189 (7), 173 (3), 95 (14), 81 (23), 70 (100), 67 (24), 55 (30).

β. Preparation of trans-4-oxa-9-thiabicyclo[5.3.0]decane 9,9-dioxide (420; X = 0)

To a solution of trans-4-oxa-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (418; X = 0) (10 mg, 5.4×10^{-2} mmol) in methanol (15 ml) was added 10% palladium-on-charcoal (8 mg) and the mixture hydrogenated at a pressure of one atmosphere of hydrogen for 3h. TLC (silica; ether) analysis indicated the absence of starting sulphone (418; X = 0) (R_f 0.50) and only a single product spot (R_f 0.08). Following removal of the catalyst by filtration, evaporation of the filtrate under reduced pressure afforded a colourless crystalline solid, trans-4-oxa-9-thiabicyclo-[5.3.0]decane 9,9-dioxide (420; X = 0) (10 mg, 98%), m.p. 95-97°C on recrystallisation from methylene chloride/diisopropyl ether.

EA: $C_8H_{14}O_3S$ requires 50.5% C, 7.4% H; found 50.5% C, 7.2% H; ^1H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.52-2.11 (m; 4H), 2.15-2.53 (m; 2H), 2.64-2.97 (m; 2H), 3.23-3.48 (m; 2H), 3.51-3.99 (m; 4H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 34.14 (CH_2), 41.22 (CH), 58.97 (CH_2), 67.27 (CH_2); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1329, 1308, 1280 (SO_2), 1255, 1229, 1157, 1134, 1112 (SO_2), 1096, 1045, 1021, 800; MS [EI] m/e (%):

190 (4; M^+), 189 (5), 173 (2), 170 (2), 160 (5), 158 (3), 126 (24), 125 (25), 111 (75), 97 (37), 95 (100), 84 (89), 83 (81), 81 (79), 68 (68), 67 (71), 55 (72).

b. FVP of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thia-tetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane 5,5-dioxide (278; X = CH_2)

i. At 500°C

FVP [110°C, 500°C, 3 x 10^{-3} mm Hg] of the title compound (278; X = CH_2) (17 mg, 9.2 x 10^{-2} mmol) gave a colourless oil which was dissolved in deuteriochloroform while still cold. Analysis of this solution by GLC (10% PEGA; 100°C) indicated the presence of a very small amount of a single volatile product. Although not identified, GC-MS indicated this to be a C_9H_{12} hydrocarbon: GC-MS [EI] m/e (%): 120 (12; M^+), 105 (23), 91 (42), 79 (94), 78 (31), 77 (57), 66 (100), 51 (26), 41 (45), 40 (23), 39 (71). TLC (silica; ether) indicated the presence of a single component, R_f 0.58. Evaporation of the product solution gave cis-9-thiabicyclo[5.3.0]-deca-2,5-diene 9,9-dioxide (416; X = CH_2) (17 mg, 100%) as a colourless semi-solid which could not be induced to crystallise.

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.91-3.56 (m; 8H), 5.42-5.93 (m; 4H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 28.45 (CH_2), 40.36 (2 x CH), 58.56 (2 x CH_2), 128.69 (2 x CH), 129.73 (2 x CH); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1647, 1403, 1319, 1301, 1290 (SO_2), 1268, 1246, 1215, 1120 (SO_2), 1106, 900, 813, 801, 698, 659; MS [EI] m/e (%): 184 (5; M^+), 170 (10), 119 (90), 118 (53), 105 (92), 92 (38), 91 (74), 79 (52), 78 (81), 77 (60), 67 (100).

ii. At 400°C

FVP [102°C, 400°C, 5 x 10^{-3} mm Hg] of the title compound (278; X = CH_2) (6 mg, 3.3 x 10^{-2} mmol) gave a colourless oil which was dissolved whilst still cold in deuteriochloroform. ^1H NMR spectroscopic analysis of the resultant solution indicated the presence of starting sulphone (278; X = CH_2) (37%) and cis-9-thiabicyclo[5.3.0] deca-2,5-diene 9,9-dioxide (416; X = CH_2) (62% yield) - confirmed by TLC (silica; ether) analysis. GLC (10% PEGA; 100°C) established the presence of a trace amount of the C_9H_{12} hydrocarbon found earlier on FVP of (278; X = CH_2) at 500°C.

iii. At 600°C

FVP [115°C, 600°C, 5 x 10^{-3} mm Hg] of the title compound (278; X = CH_2) (6 mg, 3.3 x 10^{-2} mmol) gave a pyrolysate of a light yellow oil which was dissolved, whilst still cold, in deuteriochloroform. Analysis and quantification of the products by ^1H NMR spectroscopy indicated the presence of cis-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = CH_2) (ca 96%). GLC (10% PEGA; 100°C) analysis indicated the presence of the same C_9H_{12} hydrocarbon found on pyrolysis at lower temperatures together with eight other minor volatile components, each determined to be C_9H_{12} hydrocarbons from GC-MS examinations.

iv. At 700°C

FVP [120°C, 700°C, 4 x 10^{-3} mm Hg] of the title compound (278; X = CH_2) (3 mg, 1.6 x 10^{-2} mmol) gave a light yellow oil. Dissolution of this material, while cold, in deuteriochloroform and calibration of the ^1H NMR spectrum of the resultant solution by addition of methylene chloride (1.2 mg) allowed identification of

cis-9-thiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = CH_2) (ca 45% yield). Unidentified signals in the proton spectrum corresponded to the volatile products formed - GLC (10% PEGA; 100°C) confirmed the presence of increased (equal) quantities of the nine C_9H_{12} products evident on pyrolysis of (278; X = CH_2) at 600°C.

c. FVP of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5,10-dithiatetracyclo[7.1.0.$0^{2,8}$.$0^{3,7}$]decane 5,5-dioxide (278; X = S)

i. At 600°C

FVP [125°C, 600°C, 4 x 10^{-3} mm Hg] of the title compound (278; X = S) (59 mg, 0.29 mmol) gave a pyrolysate comprising a yellow oil and a colourless polymeric solid. Addition of deuteriochloroform (0.6 ml) followed by filtration (to remove the insoluble polymeric material) gave a solution found on analysis by GLC (5% SE 30; 55°C) to contain minor quantities of benzene, toluene, o-xylene and styrene. In addition to these volatile components, capillary GC-MS indicated that three non-volatile products were also present. The GC-MS data was found to be fully in accord with the two sulphone products below, and the third (unidentified) product was found to possess a molecular formula of $C_8H_{10}S$:- MS [GC-MS] m/e (%): 138 (22; M^+), 135 (10), 123 (7), 110 (9), 105 (18), 97 (12), 91 (18), 85 (13), 83 (15), 79 (14), 77 (15), 60 (19), 42 (21), 40 (42), 38 (64), 36 (100).

TLC (silica; ether) analysis demonstrated the presence of two product bands , R_f 0.82 and 0.45. A yellow oil (33 mg) was obtained on evaporation of the pyrolysate solution and this was separated by preparative TLC (silica; ether) to give the two bands. The first, obtained as a deep-yellow, foul-smelling oil (4 mg), displayed a

complex ^1H NMR spectrum in accord with a mixture of unsaturated products. The second band was realised as a colourless crystalline solid (8 mg), identified as a 1:5 molar ratio of cis-8-thiabicyclo-[4.3.0]nona-2,4-diene 8,8-dioxide (212) (est. 1.2 mg, 2%) [from a comparison of ^1H and ^{13}C DEPT NMR spectra with those of an authentic sample] and cis-4,9-dithiabicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = S) (est. 6.8 mg, 12%). Re-examination of the ^1H and ^{13}C DEPT NMR spectra of the crude pyrolysate revealed the presence of (212) and (416; X = S) in 3% and 18% yields respectively.

EA: 5:1 molar ratio (85.6 : 14.4 weight ratio) of (416; X = S) ($C_8H_{10}O_2S_2$): (212) ($C_8H_{10}O_2S$) requires 48.8% C, 5.1% H; found 49.0% C, 4.7% H; ^1H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.08-3.32 (m; 4H), 3.40-3.70 (m; 2H), 5.70-6.30 (m; 4H) [(416; X = S) only]; ^{13}C DEPT NMR ($CDCl_3$; 80 MHz) δ [ppm]: 41.35 (CH), 58.01 (CH_2), 123.93 (CH), 127.27 (CH) [(416; X = S) only]; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1607, 1411, 1333, 1295 (SO_2), 1268, 1243, 1206, 1116 (SO_2), 872, 787, 764, 721, 692; MS [GC-MS] m/e (%): 202 (22; M^+), 137 (24), 136 (29), 123 (16), 105 (28), 97 (29), 91 (22), 85 (41), 79 (19), 78 (13), 77 (24), 53 (21), 45 (42), 32 (24), 28 (100) [(416; X = S) only].

ii. At 500°C

FVP [125°C, 500°C, 5 x 10^{-3} mm Hg] of the title compound (278; X = CH_2) (13 mg, 6.4 x 10^{-2} mmol) gave a pyrolysate consisting of a colourless solid and light yellow liquid. On addition of deuteriochloroform (0.6 ml) to the cold products, a small quantity of insoluble polymeric solid was filtered off and the filtrate analysed by ^1H NMR spectroscopy. This indicated the presence of starting sulphone (278; X = S) (est. 10% recovered), cis-8-thiabicyclo[4.3.0]-nona-2,4-diene 8,8-dioxide (212) (est. 5% yield) and cis-4,9-dithia-

bicyclo[5.3.0]deca-2,5-diene 9,9-dioxide (416; X = S) (est. 28% yield). GLC (5% SE 30; 55°C and 220°C) analysis indicated a similar ratio of the four aromatic hydrocarbons and $C_8H_{10}S$ product (present in lower combined yield) as found for FVP of (278; X = CH_2) at 600°C.

3. FVP of a transoid,transoid-5-thiatetracyclo[7.2.0.0^{2,8}.0^{3,7}]-undecane 5,5-dioxide system: dimethyl (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thiatetracyclo[7.2.0.0^{2,8}.0^{3,7}]-undecane-exo-cis-10,11-dicarboxylate 5,5-dioxide (306)

a. At 300°C

FVP [170°C, 300°C, 6 x 10^{-3} mm Hg] of the title compound (306) (3 mg, 1 x 10^{-2} mmol) gave a colourless crystalline pyrolysate. Analysis of this by ^{1}H NMR spectroscopy (in deuteriochloroform) with calibration by addition of methylene chloride (2.4 mg) allowed identification and quantification of starting sulphone (306) (est. 90% recovered). No other products were observed.

b. At 500°C

FVP [150-200°C, 500°C, 4 x 10^{-3} mm Hg] of the title compound (306) (100 mg, 0.32 mmol) gave a mixture of a light yellow oil and solid. Upon addition of deuteriochloroform (0.6 ml) to the cold mixture, a colourless polymeric solid which remained insoluble was removed by filtration. Examination of the pyrolysate by GLC (5% SE 30; 100°C) indicated the presence of 12 volatile products, two of which predominated; none of these were identified.

TLC (silica; ether) analysis demonstrated the absence of starting sulphone (306) and presence of four product components, R_f 0.22 (main), 0.37, 0.48 and 0.78. Evaporation of the product solution gave a light yellow oil (56 mg) which was separated into the four components by preparative TLC (silica; ether) giving:

(i) R_f 0.22, a colourless oil - distilled at 140-150°C, 0.02 mm Hg to give a 3:1 isomeric mixture of methyl (E)-2-(methyl vinylene-carboxylate)-cis-8-thiabicyclo[4.3.0]non-4-ene-3-carboxylate 8,8-dioxides (432) (17 mg, 17%).

EA: $C_{14}H_{18}O_6S$ requires 53.5% C, 5.8% H; found 53.3% C, 5.9% H; ^{1}H NMR ($CDCl_3$; 400 MHz) δ [ppm] (major isomer only): 2.54 (sym m; H_1), 2.92-3.02 (m; H_2,H_{7a}), 3.11-3.35 (cm; H_3, H_{7b}, H_{9a}, H_{9b}), 3.62 (s; C(13)H_3), 3.72 (s; C(12)H_3), 4.04 (q, $J_{1,6} = J_{5,6} = J_{6,7} = 8$ Hz; H_6), 5.80-5.91 (m; H_4, H_5), 6.00 (d, $J_{10,11} = 13$ Hz; H_{11}), 6.59 (dd, $J_{10,11} = 13$ Hz, $J_{2,10} = 8$ Hz; H_{10}) [assignments of signals to protons, and of coupling constants were made by reference to the ^{1}H-2D COSY spectrum]; ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]:- major isomer: 34.30, 36.18, 36.80, 46.75, 51.51, 52.07, 54.14, 54.45, 123.72, 125.91, 126.48, 145.65, 165.81 (Q), 171.93 (Q); minor isomer: 34.76, 37.05, 38.99, 46.75, 51.58, 52.22, 54.66, 55.19, 125.43, 125.76, 126.97, 145.84, 165.92 (Q), 171.75 (Q); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 3000, 2946, 1721 (CO), 1645, 1436, 1411, 1298 (SO_2), 1276, 1197, 1122 (SO_2), 1029, 989, 912, 823, 728; MS [FAB] m/e (%): 314 (80; M^+), 282 (68), 254 (15), 250 (23), 223 (54), 222 (100), 189 (20), 157 (41), 131 (71), 91 (96), 77 (61).

(ii) R_f 0.37, a colourless oil (6 mg). Analysis by ^{1}H NMR spectroscopy indicated the presence of complicated signals in the olefinic region (δ 5.52-6.15), a signal due to a methyl ester resonance (δ 3.73) and a complex range of signals in the saturated region (δ 2.70-4.45) in accord with an unsaturated sulpholane - methyl ester product or products (unidentified).

(iii) R_f 0.48, a light yellow oil (2 mg). This displayed a very similar ^{1}H NMR spectrum to that obtained in (ii) above; the IR spectrum

displayed an ester carbonyl absorption (1728 cm^{-1}) and absorptions due to the sulphone group (1296 and 1122 cm^{-1}). Again, characterisation could not be achieved due to material limitations but the product(s) appeared to be unsaturated ester/sulpholane system(s).

(iv) R_f 0.78, a colourless oil (6 mg). The ^1H NMR spectrum indicated this to contain a number of unsaturated methyl ester products (none identified) not containing a sulphone group.

c. At 400°C

FVP [180°C, 400°C, 6 x 10^{-3} mm Hg] of the title compound (306) (4 mg, 1.3 x 10^{-2} mmol) gave a pyrolysate of a colourless oil and solid. This was dissolved, while still cold, in deuteriochloroform and analysed by ^1H NMR spectroscopy which indicated the presence of starting sulphone (306) (est. 39%) and an equimolar amount of unsaturated methyl ester/sulpholane products (assumed isomeric to (306)) which remain unidentified. TLC (silica; ether) analysis confirmed the presence of starting sulphone (306) (R_f 0.14) and also indicated the presence of the three components R_f 0.37, 0.48 and 0.78 also found for FVP of (306) at 500°C. Analysis by GLC (5% SE 30; 100°C) demonstrated the presence of seven volatile components (also present in the pyrolysate at 500°C) in minor quantities. None of these were identified.

4. FVP of transoid,transoid-11-thiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]-dodecane 11,11-dioxide based systems

a. FVP of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylic heterocyclic systems (446)

i. Pyrolysis of N-phenyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboximide 4,4-dioxide (354) and derived pyrolysis products

∝. Vertical vacuum pyrolysis (VVP) of N-phenyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboximide 4,4-dioxide (354)

VVP [600°C, 5 x 10^{-3} mm Hg] of the title compound (354) (0.189 g, 0.60 mmol) was carried out by dropping the material, in ca 20 equal portions, over a 2 min period into the hot zone. A pyrolysate of a colourless crystalline solid and a yellow oil was obtained, and this was dissolved in methylene chloride and evaporated to give a light yellow oil (0.146g). GLC (5% SE 30; 220°C) and GC-MS analyses indicated the presence of three isomeric $C_{16}H_{15}NO_2$ structures (M^+=253) in 67%, 4% and 26% yields in order of increasing t_R.

The highest t_R component was separated by crystallisation from methylene chloride/diisopropyl ether to give pure N-phenyl cycloocta-(Z,Z)-3,7-diene-exo-cis-1,2-dicarboximide (449; X = NPh) (29 mg, 19%) as fine colourless needles, m.p. 164-167°C.

EA: $C_{16}H_{15}NO_2$ requires 75.9% C, 6.0% H, 5.5% N; found 76.2% C, 6.0% H, 5.7% N; ^{1}H NMR ($CDCl_3$; 360 MHz) δ [ppm]: 2.15-2.24 (cm; H_{5b}, H_{6b}), 2.47-2.55 (cm; H_{5a}, H_{6a}), 4.13-4.14 (sym m; H_1, H_2), 5.71-5.83 (cm; H_3, H_8, H_4, H_7), 7.28-7.31 (cm; 2H), 7.36-7.41 (cm; 1H), 7.44-7.49 (cm; 2H) [proton assignments were made by reference to ^{1}H selectively decoupled and NOE NMR spectra which also permitted evaluation of the following coupling constants: $J_{1,3}$ ($J_{2,8}$) = 1.1 Hz, $J_{1,7}$ ($J_{2,4}$) = 0.7 Hz, $J_{1,8}$ ($J_{2,3}$) = 2.4 Hz, $J_{3,4}$ ($J_{7,8}$) = 10.9 Hz, $J_{3,5a}$ ($J_{6a,8}$) = 1.1 Hz, $J_{4,5a}$ ($J_{6a,7}$) = 4.5 Hz, $J_{4,5b}$ ($J_{6b,7}$) = 6.0 Hz]; ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 27.69 (2 x C), 45.97 (2 x C), 123.01 (2 x C), 126.29 (2 x C), 128.46 (C), 129.01 (2 x C), 131.89 (Q), 132.50 (2 x C), 177.23 (2 x Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1707 (CO), 1502, 1493, 1391, 1382, 1288, 1261, 1190, 1171, 814, 749, 688; MS [EI] m/e (%): 253 (100; M^+), 225 (18), 174 (5), 173 (5), 134 (25), 119 (13), 106 (74), 91 (52), 78 (98).

The recrystallisation filtrate, now depleted in content of the highest t_R component (449; X = NPh) could not be further resolved to give the other two isomeric products in pure form: TLC (silica; ether) demonstrated a single spot, R_f 0.64; TLC (alumina; ether) gave a single spot, R_f 0.83, for the three isomers. An attempted separation by preparative GLC (10% SE 30, 250°C) failed due to the involatility of the three components. However, the two remaining isomers were identified as N-phenyl trans/cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboximides (450; X = NPh) [67%]/(451; X = NPh) [4% yield] from the following analytical data:

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.11-2.36 (bd m; 2H), 2.82-3.47 (m; 2H), 3.59 (dist dd, J = 7 Hz, 2.5 Hz; 1H), 5.05-5.34 (m; 2H), 5.77-6.26 (m; 3H), 7.14-7.55 (m; 5H) [major isomer (450; X = NPh) only]; ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]:- major isomer (450; X = NPh): 26.93 (CH_2), 35.46 (CH), 40.83 (CH), 44.09 (CH), 115.32 (CH_2), 121.34 (CH), 126.17 (2 x CH), 128.21 (CH), 128.81 (CH), 128.91 (2 x CH), 131.86 (Q), 139.13 (CH), 175.63 (Q), 176.64 (Q); minor isomer (451; X = NPh): 27.87 (CH_2), 37.89 (CH), 41.93 (CH), 43.94 (CH), 116.74 (CH_2), 123.26 (CH), 126.17 (2 x CH), 128.21 (CH), 128.83 (2 x CH), 129.27 (CH), 134.11 (Q), 137.23 (CH), 175.49 (Q), 176.32 (Q); IR (neat film) $\nu_{max.}$ [cm^{-1}] (86:5:9 mixture of (450; X = NPh), (451; X = NPh) and (449; X = NPh)): 2925, 2855, 1778, 1710 (CO), 1596, 1398, 1376, 1260, 1177, 914, 796, 749, 691; MS [GC-MS] m/e (%):- major isomer (450; X = NPh): 253 (18; M^+), 133 (9), 119 (21), 106 (92), 91 (100), 79 (26), 78 (91), 77 (38), 51 (18); minor isomer (451; X = NPh): 253 (26; M^+), 119 (76), 106 (91), 79 (46), 78 (100), 77 (55).

β. FVP of N-phenyl-(cis-1-transoid-1,2-cis-2)-4-thiatricyclo-[5.2.0.0^{2,6}]nonane-exo-cis-8,9-dicarboximide 4,4-dioxide (354)

FVP [200°C, 650°C, 3 x 10^{-3} mm Hg] of the title compound (354) (4 mg, 1.3 x 10^{-2} mmol volatilised - 8 mg charred residue) gave a pyrolysate mixture of colourless solid and liquid. ^{1}H NMR and GLC (5% SE 30; 220°C) analyses indicated the presence (in order of increasing t_R) of N-phenyl trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboximide (450; X = NPh) (85% yield), N-phenyl cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboximide (451; X = NPh) (5%) and N-phenyl cycloocta-(Z,Z)-3,7-diene-exo-cis-1,2-dicarboximide (449; X = NPh) (4%).

γ. FVP of N-phenyl cycloocta-(Z,Z)-3,7-diene-exo-cis-1,2-dicarboximide (449; X = NPh)

FVP [120°C, 650°C, 4 x 10^{-3} mm Hg] of the title compound (449; X = NPh) (3.1 mg, 1.2 x 10^{-2} mmol) gave a mixture of colourless solid and oil. This was dissolved in deuteriochloroform - analysis by ^{1}H NMR spectroscopy and GLC (5% SE 30; 220°C) concluded that the product comprised N-phenyl trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboximide (450; X = NPh) (76% yield), N-phenyl cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboximide (451; X = NPh) (7%) and N-phenyl cycloocta-(Z,Z)-3,7-diene-exo-cis-1,2-dicarboximide (449; X = NPh) (7%).

δ. FVP of a mixture of N-phenyl trans/cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboximide (450; X = NPh)/(451; X = NPh) and N-phenyl cycloocta-(Z,Z)-3,7-diene-exo-cis-1,2-dicarboximide (449; X = NPh)

FVP [120°C, 650°C, 5 x 10^{-3} mm Hg] of an 82 : 6 : 12 mixture of the title compounds (450; X = NPh), (451; X = NPh) and (449; X = NPh) (37 mg, 0.15 mmol) gave a light yellow oil (36 mg, 97%) found to consist of a 96 : 3 : 1 mixture of these three starting imides following analysis by ^{1}H NMR spectroscopy and GLC (5% SE 30; 220°C).

ii. FVP of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a)

α. FVP of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$]-nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a) at 650°C

FVP [240°C, 650°C, 5 x 10^{-3} mm Hg] of the title compound (242a) (73 mg, 0.30 mmol) gave a yellow oil (56 mg), purified by microdistillation at 100-103°C, 0.02 mm Hg to yield a slightly yellow oil (51 mg). Spectroscopic and GLC (5% SE 30; 170°C) analyses were in accord with a 68 : 26 : 6 mixture of the following $C_{10}H_{10}O_3$ isomeric products:

(i) trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic anhydride (450; X = O) (est. 34.4 mg, 64% yield) - this compound was obtained in pure form, as described later (p.552).

(ii) cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic anhydride (451; X = O) (est. 13.4 mg, 25% yield):- ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.14-2.42 (m; H_{5a}, H_{5b}), 2.64-2.77 (m; H_6), 3.44 (dd, $J_{1,2}$ = 8.6 Hz, $J_{1,6}$ = 4.8 Hz; H_1), 3.63-3.75 (m; H_2), 5.14-5.23 (m; H_{8a}, H_{8b}), 5.73-5.87 (m; H_4), 6.00-6.13 (m; H_3, H_7) [assignments of protons to signals aided by analogy to (450; X = O)]; ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 26.97 (CH_2), 36.48 (CH), 42.59 (CH), 44.65 (CH), 117.73 (CH_2), 119.11 (CH), 130.97 (CH), 136.50 (CH), 178.06 (Q), 179.12 (Q).

(iii) cycloocta-(Z,Z)-3,7-diene-cis-1,2-dicarboxylic anhydride (449; X = O) (est. 3.2 mg, 6%):- ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.08-2.30 (m; 4H), 4.22 (bd s; 2H), 5.65-5.89 (m; 4H); ^{13}C DEPT NMR ($CDCl_3$;

50.3 MHz) δ [ppm]: 23.58 (CH_2), 45.99 (CH), 120.82 (CH), 133.42 (CH) [NMR data also derived from examination of the pyrolysate obtained on FVP of (242a) at 500°C - see below].

The following analytical data was obtained from the 68 : 26 : 6 mixture of (450; X = 0), (451; X = 0) and (449; X = 0):- IR (neat film) $\nu_{max.}$ [cm^{-1}]: 3078, 3040, 2974, 2924, 2892, 2840, 1863, 1779, 1641, 1434, 1420, 1208, 1081, 1042, 993, 947, 929, 910, 842, 798, 763, 677; MS [EI] m/e (%): 178 (4; M^+: expected for $C_{10}H_{10}O_3$ 178.062989, found 178.063858 - error < 5 ppm), 150 (1), 134 (1), 106 (100), 105 (30), 91 (96), 79 (37), 78 (98), 77 (33), 51 (32), 39 (41).

β. FVP of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.$0^{2,6}$] nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a) at 500°C

FVP [210°C, 500°C, 6 x 10^{-3} mm Hg] of the title compound (242a) (24 mg, 0.10 mmol) gave a pyrolysate consisting of a colourless solid and light yellow oil. Following addition of deuteriochloroform, the insoluble solid present was recovered and identified by examination of IR and melting-point data as starting anhydride (242a) (4 mg, 17% recovered). Analysis of the deuteriochloroform solution by ^1H NMR spectroscopy indicated the presence of trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic anhydride (450; X = 0) (est. 35% yield), cis-6-vinyl-cyclohex-3-ene-cis-1,2-dicarboxylic anhydride (451; X = 0) (est. 14% yield) and cycloocta-(Z,Z)-3,7-diene-cis-1,2-dicarboxylic anhydride (449; X = 0) (est. 29% yield).

γ. Preparation of trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic anhydride (450; X = 0)

γ1. trans-6-Vinylcyclohex-3-ene-cis-1,2-dicarboxylic acid (456)

A mixture of trans/cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic anhydrides (450; X = O)/(451; X = O) and cycloocta-(Z,Z)-3,7-diene-cis-1,2-dicarboxylic anhydride (449; X = O) (0.225g, 1.26 mmol; 68 : 26 : 6 ratio [from FVP of (242a) at 650°C]) in water (10 ml) was stirred at room temperature, forming a colourless solid after a few minutes. After 11h, the mixture was heated under reflux for 30 min and the resultant solution hot filtered to remove a small quantity of brown solid. On slow cooling, small elongated colourless crystals were formed. These were filtered off, washed with further water and dried in vacuo (room temperature, 0.1 mm Hg) to give pure trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic acid (456) (61 mg, 36% yield on available (450; X = O)), m.p. 156-159°C.

EA: $C_{10}H_{12}O_4$ requires 61.2% C, 6.2% H; found 61.4% C, 6.1% H; ^{1}H NMR (CD_3SOCD_3; 360 MHz) δ [ppm]: 1.94 (AB pattern: bd d, $J_{5a,5b}$ = 18.3 Hz; H_{5a}) and 2.09 (AB pattern: ddt, $J_{5a,5b}$ = 18.3 Hz, $J_{5b,6}$ = 8.3 Hz, $J_{2,5b}$ = $J_{4,5b}$ = 2.9 Hz; H_{5b}), 2.88-2.93 (m; H_1, H_6), 3.06 (ddt, $J_{2,5a}$ = 7.3 Hz, $J_{1,2}$ = 5.3 Hz, $J_{2,4}$ = $J_{2,5b}$ = 2.9 Hz; H_2), 5.04 (dt, $J_{7,8a}$ = 10.2 Hz, $J_{6,8a}$ = $J_{8a,8b}$ = 1.3 Hz; H_{8a}), 5.09 (dt, $J_{7,8b}$ = 17.3 Hz, $J_{6,8b}$ = $J_{8a,8b}$ = 1.3 Hz; H_{8b}), 5.65 (dq, $J_{3,4}$ = 10.6 Hz, $J_{2,4}$ = $J_{4,5a}$ = $J_{4,5b}$ = 2.9 Hz; H_4), 5.83-5.92 [cm: comprises 5.86 (d, $J_{3,4}$ = 10.6 Hz; H_3) and 5.88 (ddd, $J_{7,8b}$ = 17.3 Hz, $J_{7,8a}$ = 10.2 Hz, $J_{6,7}$ = 6.2 Hz; H_7], 12.23 (bd s; 2H) - assignments made by reference to decoupled ^{1}H NMR spectra; ^{13}C NMR and ^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 26.78 (CH_2), 36.43 (CH), 39.42 (CH), 45.18 (CH), 114.57 (CH_2), 124.09 (CH), 125.23 (CH), 140.61 (CH), 173.22 (Q), 173.33 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 3300-2400 (OH), 1708 (CO), 1421, 1316, 1301, 1248, 997, 951, 926, 711, 678; MS [EI] m/e (%): 196 (3; M^+),

178 (26), 160 (9), 150 (21), 132 (12), 106 (54), 105 (100), 91 (59), 79 (53), 78 (36), 77 (38).

Evaporation in vacuo of the aqueous filtrate gave a light yellow crystalline solid (0.157g) found on analysis by ^{1}H and ^{13}C DEPT NMR to be an approximately 2:1 mixture of trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic acid (456) (est. 0.105g - total 0.166g, 99% yield on available anhydride (450; X = O)) and cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic acid (457) (est. 52 mg, 81% yield on available anhydride (451; X = O)) [^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 26.94 (CH_2), 39.03 (CH), 43.29 (CH), 44.73 (CH), 113.93 (CH_2), 124.17 (CH), 125.63 (CH), 141.12 (CH)].

γ2. trans-6-Vinylcyclohex-3-ene-cis-1,2-dicarboxylic anhydride (450; X = O)

A mixture of trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic acid (456) (33 mg, 0.17 mmol) in acetic anhydride (2 ml) was heated and stirred at 50°C for 1h. Evaporation of the resultant solution at 35°C, 0.5 mm Hg gave as a slightly yellow oil, trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic anhydride (450; X = O) (28 mg, 93%).

^{1}H NMR ($CDCl_3$; 250 MHz) δ [ppm]: 2.06 (dist dddd, $J_{5a,5b}$ = 18.0 Hz, $J_{5a,6}$ = 5.9 Hz, $J_{3,5a}$ = 4.2 Hz, $J_{4,5a}$ = 1.9 Hz; H_{5a}), 2.27 (dist dddd, $J_{5a,5b}$ = 18.0 Hz, $J_{5b,6}$ = 5.9 Hz, $J_{3,5b}$ = 4.2 Hz, $J_{4,5b}$ = 1.9 Hz; H_{5b}), 2.78 (quintet x d, $J_{1,6} = J_{5a,6} = J_{5b,6} = J_{6,7}$ = 5.9 Hz, $J_{6,8b}$ = 0.5 Hz; H_6), 3.20 (dd, $J_{1,2}$ = 8.5 Hz, $J_{1,6}$ = 5.9 Hz; H_1), 3.67 (ddd, $J_{1,2}$ = 8.5 Hz, $J_{2,4}$ = 3.9 Hz, $J_{2,3}$ = 2.3 Hz; H_2), 5.14 (ddd, $J_{7,8b}$ = 17.5 Hz, $J_{8a,8b}$ = 0.9 Hz, $J_{6,8b}$ = 0.5 Hz; H_{8b} [overlaps with H_{8a} signal]), 5.15 (dd, $J_{7,8a}$ = 10.3 Hz, $J_{8a,8b}$ = 0.9 Hz; H_{8a} [overlaps with H_{8b} signal]), 5.79 (ddt, $J_{3,4}$ = 10.0 Hz, $J_{2,4}$ = 3.9 Hz,

$J_{4,5a} = J_{4,5b} = 1.9$ Hz; H_4 [lies within H_7 signal]), 5.81 (ddd, $J_{7,8b} = 17.5$ Hz, $J_{7,8a} = 10.3$ Hz, $J_{6,7} = 5.9$ Hz; H_7), 6.03 (dtd, $J_{3,4} = 10.0$ Hz, $J_{3,5a} = J_{3,5b} = 4.2$ Hz, $J_{2,3} = 2.3$ Hz; H_3) - assignments made by reference to ^1H decoupled and ^1H-2D NOESY NMR spectra; ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 26.82 (CH_2), 35.27 (CH), 40.95 (CH), 44.30 (CH), 116.57 (CH_2), 118.87 (CH), 130.00 (CH), 137.63 (CH), 170.42 (Q), 171.37 (Q); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 3085, 3048, 2895, 2844, 1867 (CO), 1784 (CO), 1423, 1207, 1082, 1043, 993, 912, 763, 677; MS [EI] m/e (%): 178 (42; M^+: calculated for $C_{10}H_{10}O_3$ 178.0630, found 178.0573), 160 (19), 150 (13), 148 (12), 107 (33), 106 (61), 105 (47), 91 (100), 79 (50), 78 (89), 77 (53), 51 (48), 39 (46), 32 (68).

δ. Preparation of dimethyl trans/cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylates (394)/(395) and dimethyl cycloocta-(Z,Z)-3,7-diene-cis-1,2-dicarboxylate (392)

A solution of trans/cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic anhydrides (450; X = O)/(451; X = O) and cycloocta-(Z,Z)-3,7-diene-cis-1,2-dicarboxylic anhydride (449; X = O) (69.1 mg, 0.39 mmol; 68 : 26 : 6 ratio [obtained from FVP of (242a) at 650°C]) in methanol (2 ml) containing concentrated sulphuric acid (15 mg) was heated under reflux for 2h. TLC (silica; ether) analysis of the product solution indicated the presence of a single UV-active spot (R_f 0.70) and this material was isolated following column chromatography (silica; ether) to give a yellow oil (43.5 mg). Microdistillation of this at 98-102°C, 0.35 mm Hg yielded a colourless oil, identified as a mixture of dimethyl trans/cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylates (394)/(395) and dimethyl cycloocta-(Z,Z)-3,7-diene-cis-1,2-dicarboxylate (392) (39.7 mg, 46%), respectively 70 : 25 : 5 from ^1H NMR analysis.

EA: $C_{12}H_{16}O_4$ requires 64.3% C, 7.2% H; found 64.2% C, 7.3% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 1.97 and 2.10 (AB pattern, bd d, J = 17 Hz; 2H), 2.96-3.10 (cm; 2H), 3.22-3.34 (m; 1H), 3.64 (s; 3H), 3.68 (s; 3H), 5.02-5.19 (cm; 2H), 5.71-6.02 (cm; 3H) [major isomer (394) only]; ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]:- (394): 27.68 (CH_2), 36.61 (CH), 40.31 (CH), 46.03 (CH), 51.65 (CH_3), 51.88 (CH_3), 115.39 (CH_2), 122.76 (CH), 126.90 (CH), 139.64 (CH), 172.82 (2xQ); (395): 27.43 (CH_2), 36.61 (CH), 39.63 (CH), 39.79 (CH), 51.88 (CH_3), 52.02 (CH_3), 115.60 (CH_2), 122.59 (CH), 127.37 (CH), 139.39 (CH), 172.82 (2xQ); IR (neat film) $\nu_{max.}$ [cm^{-1}]: 2952, 1743, 1202, 1038, 996, 914, 681; MS [EI] m/e (%): 224 (14; M^+), 193 (33), 192 (48), 164 (52), 106 (44), 105 (100), 104 (37), 91 (43), 79 (40), 77 (45), 59 (50).

GLC (10% PEGA; 130°C) and GC-MS analyses indicated the presence of predominantly methyl (Z)/(E)-penta-2,4-dienoates (397)/(396) [by comparison with authentic samples] together with two minor (higher t_R) peaks which exhibited fragmentation patterns similar to that found for MS under EI conditions for (394) and (395). A low intensity peak (too weak for GC-MS acquisition) was tentatively assigned to (392). The dienes (397) and (396) [not observed in the ^{1}H NMR spectrum of the product mixture] appear to arise from thermal fragmentation of the initial mixture of (394), (395) and (392) in the GC inlet port (at a temperature of 250°C).

iii. FVP of (cis-1-transoid-1,2-cis-2)-4-thiatricyclo[5.2.0.0^{2,6}]-nonane-exo-cis-8,9-dicarboxylic thioanhydride 4,4-dioxide (360)

FVP [205°C, 650°C, 5 x 10^{-3} mm Hg] of a 63:37 mixture of the title compound (360) and (cis-1-transoid-1,2-cis-2)-4-thiatricyclo-

[5.2.0.$0^{2,6}$]nonane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (242a) (61.0 mg total: 39.3 mg, 15.2 x 10^{-2} mmol (360); 21.7 mg, 9.0 x 10^{-2} mmol (242a)) gave a pyrolysate consisting of a yellow oil. This was dissolved in deuteriochloroform and analysed by ^{1}H and ^{13}C NMR spectroscopy, and by GLC (5% SE 30; 140°C) and GC-MS. In addition to the three anhydride products associated with pyrolysis of (242a) at 650°C [see p.549], three thioanhydride products were detected and provisionally assigned to trans-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic thioanhydride (450; X = S) (est. 18.8 mg, 64% yield), cis-6-vinylcyclohex-3-ene-cis-1,2-dicarboxylic thioanhydride (451; X = S) (est. 5.2 mg, 18%) and cycloocta-(Z,Z)-3,7-diene-cis-1,2-dicarboxylic thioanhydride (449; X = S) (est. 1.4 mg, 5%) [yields estimated from ^{1}H NMR following the addition of chloroform (7.0 mg) and from GLC]. No separation could be achieved by TLC.

(450; X = S):- GLC (5% SE 30; 140°C): t_R = 6.6 min; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.03-2.35 (m; 2H), 2.83 (q, J = 6.5 Hz; 1H), 3.22 (t, J = 6.5 Hz; 1H), 3.60-3.85 (cm; 1H), 4.97-5.25 (cm; 2H), 5.58-6.15 (cm; 3H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 27.52 (CH_2), 36.54 (CH), 52.95 (CH), 56.30 (CH), 116.25 (CH_2), 120.53 (CH), 129.51 (CH), 138.18 (CH); GC-MS [EI] m/e (%): 194 (3; M^+), 192 (7), 190 (14), 164 (4), 132 (11), 106 (100), 105 (24), 104 (16), 103 (17), 102 (17), 91 (82), 79 (26), 78 (86), 77 (31), 65 (11), 51 (12), 39 (15).

(451; X = S):- GLC (5% SE 30; 140°C): t_R = 12.2 min; GC-MS [EI] m/e (%): 194 (8; M^+), 192 (22), 190 (25), 164 (12), 132 (29), 106 (100), 105 (30), 104 (33), 103 (32), 102 (31), 91 (87), 79 (30), 78 (98), 77 (44), 65 (14), 51 (21).

(449; X = S):- GLC (5% SE 30; 140°C): t_R = 17.2 min; GC-MS [EI] m/e (%): 194 (4; M^+), 166 (4), 134 (12), 133 (7), 106 (100), 105 (30), 91 (55), 79 (22), 78 (74), 77 (15), 65 (11), 41 (12).

b. FVP of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-hetero-11-thiatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 11,11-dioxide systems (447)

i. (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-Oxa-11-thiatetracyclo-[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 11,11-dioxide (367)

FVP [100-105°C, 650°C, 1 x 10^{-2} mm Hg] of the title compound (367) (0.116g, 0.54 mmol) gave a pyrolysate consisting of a colourless liquid and solid. Deuteriochloroform was added to the cold pyrolysate and a small quantity of insoluble polymeric solid removed by filtration. GLC (10% PEGA; 150°C) and GC-MS analyses of the product solution were in accord with the presence of four $C_{10}H_{14}O$ isomers, the two most abundant of which were separated by preparative GLC (30% PEGA; 120°C) and positively identified. The four isomers were found at the following GLC (10% carbowax; 150°C) retention times [estimated unseparated yields listed]:

(a) t_R = 2.39 min, [2%]:- GC-MS [EI] m/e (%): 150 (2; M^+), 119 (7), 117 (7), 105 (27), 92 (20), 91 (45), 79 (55), 77 (32), 67 (100), 41 (93), 39 (86).

(b) t_R = 2.87 min, a colourless liquid identified as exo-2-vinyl-cis-8-oxabicyclo[4.3.0]non-4-ene (458; X = O) [58%]:- Exact mass: $C_{10}H_{14}O$ requires M^+ 150.1044; found 150.1045; ^{1}H NMR ($CDCl_3$; 360 MHz) δ [ppm]: 1.89 (dist ddq, $J_{3a,3b}$ = 14.7 Hz, $J_{2,3a}$ = 7.4 Hz, $J_{3a,4} = J_{3a,5} = J_{3a,6}$ = 2.5 Hz; H_{3a}), 2.06-2.16 (cm - includes 2.08 [ddt, $J_{3a,3b}$ = 14.7 Hz, $J_{3b,4}$ = 5.1 Hz, $J_{2,3b} = J_{3b,5}$ = 1.1 Hz; H_{3b}];

H_1, H_2, H_{3b}), 2.71-2.79 (bd sym m; H_6), 3.38 (dd, $J_{6,7b}$ = 9.0 Hz, $J_{7a,7b}$ = 8.1 Hz; H_{7b}), 3.76 (dist dd, $J_{9a,9b}$ = 8.8 Hz, $J_{1,9b}$ = 2.6 Hz; H_{9b}), 3.89 (dd, $J_{9a,9b}$ = 8.8 Hz, $J_{1,9a}$ = 6.2 Hz; H_{9a}), 4.00 (t, $J_{6,7a} = J_{7a,7b}$ = 8.1 Hz; H_{7a}), 5.01 (ddd, $J_{10,11a}$ = 10.3 Hz, $J_{11a,11b}$ = 1.7 Hz, $J_{2,11a}$ = 0.3 Hz; H_{11a}), 5.06 (ddd, $J_{10,11b}$ = 17.2 Hz, $J_{11a,11b}$ = 1.7 Hz, $J_{2,11b}$ = 0.8 Hz; H_{11b}), 5.63 (ddd, $J_{10,11b}$ = 17.2 Hz, $J_{10,11a}$ = 10.3 Hz, $J_{2,10}$ = 7.5 Hz; H_{10} [overlaps with H_5 signal]), 5.68 (dddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 3.8 Hz, $J_{3a,5}$ = 2.5 Hz, $J_{3b,5}$ = 1.1 Hz; H_5 [overlaps with H_{10} signal]), 5.81 (ddt, $J_{4,5}$ = 10.0 Hz, $J_{3b,4}$ = 5.1 Hz, $J_{3a,4} = J_{4,6}$ = 2.5 Hz; H_4) - assignments of signals and coupling constants made on the basis of data available from ^{1}H NMR selective decoupling and ^{1}H-2D NOESY studies; ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 29.99 (CH_2), 38.93 (CH), 39.04 (CH), 41.04 (CH), 71.94 (CH_2), 72.57 (CH_2), 114.82 (CH_2), 125.50 (CH), 127.04 (CH), 141.57 (CH); IR ($CDCl_3$) $\nu_{max.}$ [cm^{-1}]: 3075, 3018, 2960, 2915, 2864, 1596, 1292, 1253, 1148; GC-MS [EI] m/e (%): 150 (2; M^+), 132 (4), 119 (23), 105 (92), 91 (88), 79 (100), 78 (46), 77 (61), 67 (49), 41 (60), 39 (74), 28 (66).

(c) t_R = 3.26 min, a colourless liquid identified as endo-2-vinyl-cis-8-oxabicyclo[4.3.0]non-4-ene (459; X = 0) [16%]:- ^{1}H NMR ($CDCl_3$; 360 MHz) δ [ppm]: 1.98-2.05 (cm; H_{3a}, H_{3b}), 2.59-2.65 (cm; H_1, H_2), 2.79-2.85 (bd sym m; H_6), 3.59 (t, $J_{1,9b} = J_{9a,9b}$ = 8.4 Hz; H_{9b}), 3.60 (dd, $J_{7a,7b}$ = 8.3 Hz, $J_{6,7b}$ = 2.0 Hz; H_{7b}), 3.79 (t, $J_{1,9a} = J_{9a,9b}$ = 8.4 Hz; H_{9a}), 3.84 (dd, $J_{7a,7b}$ = 8.3 Hz, $J_{6,7a}$ = 6.1 Hz; H_{7a}), 4.98 (dt, $J_{10,11a}$ = 10.5 Hz, $J_{2,11a} = J_{11a,11b}$ = 1.5 Hz; H_{11a}), 5.02 (dt, $J_{10,11b}$ = 17.3 Hz, $J_{2,11b} = J_{11a,11b}$ = 1.5 Hz; H_{11b}), 5.56 (dqd, $J_{4,5}$ = 10.0 Hz, $J_{3a,4} = J_{3b,4} = J_{4,6}$ = 2.6 Hz, $J_{2,4}$ = 1.0 Hz; H_4), 5.75 (ddd, $J_{10,11b}$ = 17.3 Hz, $J_{10,11a}$ = 10.5 Hz, $J_{2,10}$ = 6.1 Hz; H_{10}

[overlaps with H_5 signal]), 5.79 (dq, $J_{4,5}$ = 10.0 Hz, $J_{3a,5}$ = $J_{3b,5}$ = $J_{5,6}$ = 2.4 Hz; H_5 [overlaps with H_{10} signal]) - assignments of signals and coupling constants made by reference to ^1H selectively decoupled NMR spectra; ^{13}C DEPT NMR ($CDCl_3$; 90.6 MHz) δ [ppm]: 25.06 (CH_2), 37.01 (CH), 39.95 (CH), 41.16 (CH), 67.10 (CH_2), 72.95 (CH_2), 113.69 (CH_2), 126.80 (CH), 128.41 (CH), 141.60 (CH); IR ($CDCl_3$) $\nu_{max.}$ [cm^{-1}]: 2960, 2916, 2862, 1290, 1251, 1147; GC-MS [EI] m/e (%): 150 (2; M^+), 132 (2), 119 (13), 117 (12), 105 (67), 91 (84), 79 (100), 78 (44), 77 (53), 66 (44), 41 (63), 39 (82), 28 (68), 27 (41).

(d) t_R = 4.51 min, [4%]:- GC-MS [EI] m/e (%): M^+ not observed, 132 (2), 119 (7), 117 (7), 105 (24), 92 (29), 91 (43), 79 (57), 77 (33), 67 (100), 66 (31), 53 (26), 41 (76), 39 (93), 32 (74).

ii. [10,10,12,12-$^2H_4$]-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-Oxa-11-thiatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodecane 11,11-dioxide (368)

FVP [130°C, 650°C, 2 x 10^{-3} mm Hg] of the title compound (368) (20 mg, 9.2 x 10^{-2} mmol) gave a mixture of colourless oil and polymeric solid. Following addition of carbon tetrachloride to the still cold pyrolysate, the polymeric material (4 mg) was removed by filtration and the filtrate found, following GLC and GC-MS analyses, to contain four $C_{10}H_{10}D_4O$ isomers. The similarities in yields, retention times and fragmentation patterns of the products arising from FVP at 650°C of (368) and (367), allowed a parallel assignment of the two major $C_{10}H_{10}D_4O$ isomers to be made. The four isomers were located at the following retention times on GLC (10% carbowax; 150°C) [estimated yields from ^1H NMR (added chloroform) and GLC]:

(a) t_R = 2.42 min [2%]:- GC-MS [EI] m/e (%): M^+ not observed, 134 (5; $(M-D_2O)^+$), 122 (24), 121 (25), 120 (27), 109 (32), 108 (34),

107 (34), 94 (43), 93 (67), 92 (82), 94 (67), 83 (43), 82 (62), 81 (65), 80 (60), 79 (100), 78 (46), 70 (53), 69 (79), 68 (46), 55 (27), 54 (33), 53 (26), 41 (35), 40 (32), 39 (43).

(b) t_R = 2.92 min, exo-2-([2,2-$^2H_2$]-vinyl)-[3,3-$^2H_2$]-cis-8-oxabicyclo[4.3.0]non-4-ene [47%]:- ^{1}H NMR (CCl_4; 80 MHz) δ [ppm]: 2.04-2.25 (bd hump; H_1,H_2), 2.53-2.98 (bd hump; H_6), 3.38 (dd, $J_{6,7b}$ = 9.0 Hz, $J_{7a,7b}$ = 8.1 Hz; H_{7b}), 3.55-4.10 (cm; H_{9b}, H_{9a}, H_{7a}), 5.43-5.96 (bd m; H_{10}, H_5, H_4) - assignments made by analogy to (458; X = O); ^{2}H NMR (CCl_4; 30.7 MHz) δ [ppm]: 1.74-2.30 (bd hump; D_{3a}, D_{3b}), 4.95-5.20 (bd hump, D_{11a}, D_{11b}); GC-MS [EI] m/e (%): 154 (1; M^+), 153 (2), 152 (2), 151 (1), 150 (1), 137 (3), 136 (3), 135 (4), 134 (3), 133 (3), 122 (17), 121 (22), 120 (22), 119 (20), 109 (37), 108 (59), 107 (70), 106 (61), 94 (46), 93 (72), 92 (70), 82 (62), 81 (83), 80 (100), 79 (92), 78 (61), 69 (83), 68 (72), 67 (58), 53 (24), 39 (56).

(c) t_R = 3.27 min, endo-2-([2,2-$^2H_2$]-vinyl)-[3,3-$^2H_2$]-cis-8-oxabicyclo[4.3.0]non-4-ene [10%]:- GC-MS [EI] m/e (%): 154 (1; M^+), 153 (1), 152 (1), 150 (2), 137 (4), 136 (4), 135 (4), 134 (3), 133 (4), 121 (19), 119 (23), 108 (54), 107 (68), 106 (56), 94 (53), 93 (87), 92 (81), 81 (85), 80 (100), 79 (97), 78 (68), 69 (63), 68 (58), 67 (56), 66 (47), 41 (52), 39 (54).

(d) t_R = 4.54 min [5%]:- GC-MS [EI] m/e (%): M^+ not observed, 136 (5; $(M-H_2O)^+$), 135 (6), 123 (13), 121 (20), 120 (12), 109 (23), 108 (20), 107 (24), 106 (23), 105 (17), 94 (25), 93 (34), 92 (47), 91 (33), 82 (51), 81 (48), 79 (57), 69 (100), 68 (74), 53 (21), 42 (36), 39 (36).

iii. (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5,11-dithiatetracyclo-[7.3.0.0^{2,8}.0^{3,7}]dodecane 5,5-dioxide (371)

FVP [110°C, 650°C, 5 x 10^{-3} mm Hg] of the title compound (371) (35 mg, 0.15 mmol) gave a mixture of a yellow oil and brown polymeric solid. Analysis of a deuteriochloroform solution of the oil by GLC (5% SE; 140°C), GC-MS and NMR indicated the presence of three main $C_{10}H_{14}S$ isomeric products (only the major one identified) at the following retention times [yields estimated from ^{1}H NMR and GLC analyses]:

(a) 7.4 min, exo-2-vinyl-cis-8-thiabicyclo[4.3.0]non-4-ene (458; X = S) [55%]:- ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.84-2.45 (cm; 4H), 2.51-3.17 (cm; 5H), 4.89-5.25 (m; 2H), 5.44-5.86 (m; 3H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 31.09 (CH_2), 33.40 (CH_2), 36.13 (CH_2), 37.67 (CH), 43.19 (CH), 45.11 (CH), 115.41 (CH_2), 126.37 (CH), 127.23 (CH), 141.47 (CH); GC-MS [EI] m/e (%): 166 (29; M^+), 151 (3), 137 (6), 119 (54), 105 (42), 91 (62), 85 (13), 79 (26), 77 (18), 65 (15), 60 (100).

(b) 8.6 min [11%]:- GC-MS [EI] m/e (%): 166 (92; M^+), 151 (6), 138 (12), 137 (10), 119 (28), 105 (56), 99 (57), 91 (100), 85 (74), 79 (80), 65 (33), 60 (68), 41 (53).

(c) 12.3 min [5%]: GC-MS [EI] m/e (%): 166 (61; M^+), 151 (4), 137 (5), 119 (31), 105 (34), 98 (100), 97 (37), 90 (71), 84 (78), 79 (36), 78 (61), 67 (73), 65 (83), 45 (26), 41 (62).

iv. 11-Benzyl-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5-thia-11-azatetracyclo[7.3.0.02,8.03,7]dodecane 5,5-dioxide (370)

FVP [140°C, 650°C, 4 x 10^{-3} mm Hg] of the title compound (370) (64 mg, 0.21 mmol) gave a mixture of a yellow oil and polymeric

solid. Addition of deuteriochloroform to the cold pyrolysate followed by removal of the insoluble polymeric solid (2 mg) gave a product solution found by TLC (silica; ether) not to contain any starting sulphone (370) (R_f 0.16) but demonstrating product spots R_f 0.55 and 0.72. Analysis of the solution by GLC (5% SE 30; 200°C) and GC-MS indicated the presence of eight components at the following retention times [yields estimated from ^{1}H NMR and GLC analyses]:

(a) 1.28 min [1%]:- GC-MS [EI] m/e (%): 159 (14; M^+), 144 (4), 130 (3), 116 (2), 105 (4), 91 (100), 68 (13), 66 (11), 41 (7).

(b) 1.54 min [0.5%]:- GC-MS [EI] m/e (%): 159 (66; M^+), 144 (54), 130 (100), 129 (52), 116 (27), 92 (48), 79 (13), 66 (13), 41 (13), 36 (32).

(c) 1.76 min, N-benzylpyrrole (464) [9%]:- ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 6.02 (t, J = 2Hz; H_2, H_5), 6.52 (t, J = 2Hz; H_3, H_4) - similar to lit.[198] ^{1}H NMR spectrum; GC-MS [EI] m/e (%): 158 (5; $(M+1)^+$), 157 (48), 156 (4), 92 (9), 91 (100), 77 (3), 66 (21), 51 (2), 39 (4) - similar to lit.[197] mass spectrum.

(d) 2.34 min [1%]:- GC-MS [EI] m/e (%): 171 (34; M^+), 92 (8), 91 (100), 79 (2), 66 (10), 53 (2), 41 (2), 39 (2), 36 (3).

(e) 2.78 min [6%]:- GC-MS [EI] m/e (%): 183 (24; M^+), 166 (2), 104 (3), 92 (10), 91 (100), 77 (2), 66 (12), 41 (2), 39 (2).

(f) 5.06 min [0.7%]:- GC-MS [EI] m/e (%): 144 (12; $(M+1)^+$), 143 (100; M^+), 116 (13), 115 (42), 104 (4), 91 (5), 89 (5), 77 (3), 72 (5), 66 (3), 64 (2), 51 (2), 36 (3).

(g) 7.34 min, 8-benzyl-exo-2-vinyl-cis-8-azabicyclo[4.3.0]-non-4-ene (458; X = NCH_2Ph) [63%]:- ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]:

1.76-3.13 (m; 9H), 3.61 (d, J = 1.0 Hz; 2H), 4.71-5.03 (m; 2H), 5.30-5.75 (m; 3H), 6.91-7.30 (m; 5H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 29.91 (CH_2), 37.63 (CH), 39.46 (CH), 41.53 (CH), 58.46 (CH_2), 58.62 (CH_2), 59.88 (CH_2), 114.63 (CH_2), 126.63 (CH), 126.97 (CH), 127.47 (CH), 128.32 (2xCH), 129.20 (2xCH), 141.46 (CH); GC-MS [EI] m/e (%): 239 (24; M^+), 235 (9), 170 (7), 158 (9), 133 (17), 132 (15), 117 (6), 105 (8), 91 (100), 79 (8), 77 (7), 66 (8), 42 (93), 28 (89).

(h) 11.50 min [4%]:- GC-MS [EI] m/e (%): 240 (12; $(M+1)^+$), 239 (7; M^+), 237 (11), 161 (13), 149 (9), 134 (12), 121 (10), 106 (10), 92 (11), 91 (100), 79 (7), 68 (7), 42 (77).

v. (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-5,11-dithiatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodecane 5,5,11,11-tetraoxide (372)

FVP [235°C, 650°C, 1.1 x 10^{-2} mm Hg] of the title compound (372) (12 mg, 4.6 x 10^{-2} mmol) gave a colourless oil and solid product mixture. Following the addition of deuteriochloroform to the pyrolysate (whilst still cold), an insoluble polymeric solid (<1 mg) was removed by filtration and the filtrate examined by ^{1}H NMR spectroscopy and GLC (5% carbowax; 100°C). The latter indicated at least 16 volatile products to be present of which no one product predominated: only two hydrocarbons, benzene (2% yield) and toluene (1%) were identified by comparison with authentic standards. Analysis by ^{1}H NMR spectroscopy indicated the products to be largely olefinic (non sulphone-containing) in character.

c. FVP of (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-4,5-dihetero-11-thiatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodecane/ene 11,11-dioxide systems (448)

i. (cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-11-Thia-4,5-diazatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodec-4-ene 11,11-dioxide (272a)

α. At 500°C

FVP [152°C, 500°C, 5 x 10^{-3} mm Hg] of the title compound (272a) (47 mg, 0.22 mmol) gave a light yellow oil which was dissolved, whilst still cold, in deuteriochloroform. Examination of this by ^{1}H and ^{13}C DEPT NMR spectroscopy confirmed the absence of starting sulphone (272a), although an unidentified sulpholane product (est. 5% yield) was detected. This was found from capillary GC-MS to possess formula $C_9H_{12}O_2S$:- GC-MS [EI] m/e (%): 184 (2; M^+), 119 (39), 118 (32), 117 (29), 105 (38), 91 (72), 79 (100), 78 (29), 77 (42), 66 (46), 41 (38).

Analysis of the volatile components of the pyrolysate by GLC (10% PEGA; 100°C) and GC-MS indicated the presence of nine C_9H_{12} isomers; eight of these of similarly low intensity remained unidentified and accounted collectively for ca 20% yield. The major component was tentatively assigned to 3-methylene-4-vinylhexa-1,5-diene (468) (est. 65% yield):- ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.75 (tq, J = 6.5 Hz, 1.2 Hz; H_4), 4.92-5.25 (cm; 8H), 5.57-6.52 (cm; 3H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 48.27 (CH), 113.78 (CH_2), 115.43 (2xCH_2), 116.18 (CH_2), 137.70 (CH), 138.77 (2xCH); GC-MS [EI] m/e (%): 120 (4; M^+), 119 (12), 105 (63), 92 (72), 91 (100), 79 (68), 78 (24), 77 (53), 67 (41), 65 (34), 53 (54), 41 (68), 39 (71).

The product solution was found to have decomposed to give a mixture of dark brown polymeric solid and brown chloroform solution on standing at -20°C for several weeks.

β. At 400°C

FVP [138-140°C, 400°C, 6 x 10^{-3} mm Hg] of the title compound (272a) (15 mg, 7.1 x 10^{-2} mmol) gave a pyrolysate consisting of a colourless solid and light yellow oil. Following addition of deuteriochloroform, the insoluble solid which remained was removed by filtration. Analysis by IR spectroscopy verified that this was starting sulphone (272a) (4 mg, 27% recovered). Examination of the pyrolysate solution by ^{1}H NMR spectroscopy and GLC (10% PEGA; 100°C), and comparison with the products from FVP of (272a) at 500°C (see earlier) indicated the presence of the same eight minor C_9H_{12} isomers (total 15% yield on consumed (272a)) in unchanged ratio, together with a major component tentatively assigned to 3-methylene-4-vinylhexa-1,5-diene (468) (est. 70% yield on consumed (272a)).

ii. 5,endo-6-Diphenyl-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-4-oxa-11-thia-5-azatetracyclo[7.3.0.$0^{2,8}$.$0^{3,7}$]dodecane 11,11-dioxide (271a)

α. VVP at 400°C

VVP [400°C, 1-2 x 10^{-2} mm Hg] of the title compound (271a) (80 mg, 0.22 mmol) was carried out over a one min period to give a brown semi-solid pyrolysate. TLC (silica; ether) analysis indicated the presence of a major component at R_f 0.26 (UV-active) together with other (non-UV-active) components R_f 0.47, 0.51 and 0.70. The lowest R_f product was isolated by trituration of the crude product mixture with a little methylene chloride followed by recrystallisation of the insoluble crystals from methylene chloride/diisopropyl ether. Further (20 mg) of this product was obtained from preparative TLC (silica; ether) of the combined trituration and recrystallisation

filtrates to give 10,exo-11-diphenyl-(cis-1-cisoid-1,2-cis-2-transoid-2,3-cis-3)-endo-12-oxa-5-thia-10-azatetracyclo[7.2.1.$0^{2,8}$.$0^{3,7}$]dodecane 5,5-dioxide (474) (total 43 mg, 54%) as slightly brown crystals, m.p. (decomp.) 242-244°C, found to sublime cleanly at 210°C, 0.05 mm Hg.

EA: $C_{21}H_{21}NO_3S$ requires 68.6% C, 5.8% H, 3.8% N; found 68.9% C, 5.8% H, 3.7% N; ^{1}H NMR ($CDCl_3$; 250 MHz) δ [ppm]: 2.77 (dd, $J_{2,8}$ = 6.5 Hz, $J_{2,3}$ = 3.0 Hz; H_2), 2.93-3.17 (cm; H_3, H_{4a}, H_{4b}, H_{6a}, H_{6b}, H_7, H_8), 3.95 (s; H_{11}), 4.46 (s; H_1), 5.78 (s; H_9), 6.34 (d, $J_{o,m}$ = 7.9 Hz; 2 H_o [N(10)Ph]), 6.69 (t, $J_{m,p}$ = 7.4 Hz; H_p [N(10)Ph]), 7.10 (dd, $J_{o,m}$ = 7.9 Hz, $J_{m,p}$ = 7.4 Hz; 2 H_m [N(10)Ph]), 7.24-7.39 (cm; 5H[C(11)Ph]) - assignments of signals to protons, and coupling constants made by reference to ^{1}H-2D COSY, NOESY and 2D ^{1}H-^{13}C correlated NMR spectral data; ^{13}C NMR ($CDCl_3$; 62.9 MHz) δ [ppm]: 34.16 (CH), 35.39 (CH), 45.26 (CH), 45.35 (CH), 54.25 (CH_2), 54.51 (CH_2), 66.31 (CH), 87.34 (CH), 89.18 (CH), 113.21 (2xCH), 118.08 (CH), 126.56 (2xCH), 127.80 (CH), 128.77 (2xCH), 129.45 (2xCH), 140.97 (Q), 144.00 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1598, 1504, 1459, 1355, 1310 (SO_2), 1158, 1142 (SO_2), 1129, 1111, 934, 868, 807, 752, 736, 706, 699; MS [EI] m/e (%): 367 (88; M^+), 307 (8), 293 (21), 234 (100), 182 (20), 181 (25), 180 (23), 167 (19), 149 (54), 120 (40), 117 (24), 104 (67), 91 (65), 77 (94).

Analysis of the crude pyrolysate solution by GLC (5% SE 30; 150°C) indicated the presence of at least seven volatile compounds in similar concentration (none identified).

β. FVP at 400°C

FVP [160°C, 400°C, 3 x 10^{-3} mm Hg] of the title compound (271a) (7 mg, 1.9 x 10^{-2} mmol volatilised - 9 mg (dark brown oil residue) gave a pyrolysate of a light yellow solid/oil. After

dissolution in deuteriochloroform, analysis by ^{1}H NMR spectroscopy and by TLC (silica; ether) confirmed the absence of starting sulphone (271a) and indicated the presence of 10,exo-11-diphenyl-(cis-1-cisoid-1,2-cis-2-transoid-2,3-cis-3)-endo-12-oxa-5-thia-10-azatetracyclo[7.2.1.$0^{2,8}$.$0^{3,7}$]dodecane 5,5-dioxide (474) (est. 45% yield) and unidentified non-sulphone products, R_f 0.70. The inlet residue was found by ^{1}H NMR spectroscopy and TLC analysis to be of very similar composition to the pyrolysate, with no starting sulphone (271a) remaining.

γ. VVP of 10,exo-11-diphenyl-(cis-1-cisoid-1,2-cis-2-transoid-2,3-cis-3)-endo-12-oxa-5-thia-10-azatetracyclo[7.2.1.$0^{2,8}$.$0^{3,7}$]-dodecane 5,5-dioxide (474)

VVP [600°C, 2 x 10^{-2} mm Hg] of the VVP (400°C) pyrolysate of (271a) [60 mg - containing the title compound (474) (34 mg, 9.3 x 10^{-2} mmol)] gave a dark brown oil. This was dissolved (while still cold) in deuteriochloroform and examined by ^{1}H NMR spectroscopy and TLC (silica; ether) which indicated the absence of starting sulphone (474) and presence of purely aromatic unsaturated products, R_f 0.51 and 0.70. Analysis of the pyrolysate by GLC (5% SE 30; 50-220°C) showed that 12 unidentified volatile components (including the seven found in the starting material) were present.

iii. 6-(p-Methoxyphenyl)-(cis-1-transoid-1,2-cis-2-transoid-2,3-cis-3)-4-oxa-11-thia-5-azatetracyclo[7.3.0.0^{2,8}.0^{3,7}]dodec-5-ene 11,11-dioxide (270a)

α. At 450°C

FVP [180°C, 450°C, 4 x 10^{-3} mm Hg] of the title compound (270a) (20 mg, 6.3 x 10^{-2} mmol) gave a mixture of colourless solid and yellow oil. Following the addition of deuteriochloroform, the insoluble

solid product was filtered off and found, by comparison of melting point and IR spectral data, to be starting sulphone (270a) (3 mg, 15% recovered). The pyrolysate was analysed by TLC (silica; ether) which indicated the presence of two product spots at R_f 0.52 (major) and 0.42, whilst analysis by ^1H NMR spectroscopy demonstrated that a complex mixture of unsaturated (non-sulphone-containing) products had been formed. Comparison of the reported[182] ^1H NMR spectrum with the pyrolysate spectrum allowed identification of a single product, 3-(p-methoxyphenyl)-isoxazole (476) (est. 24% yield on consumed (270a)):- ^1H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.85 (s; 3H), 6.59 (d, J = 1.7 Hz; 1H), 6.97 and 7.76 (A_2B_2 pattern: d, J = 9.0 Hz; 4H), 8.40 (d, J = 1.7 Hz; 1H).

β. At 550°C

FVP [210-220°C, 550°C, 4 x 10^{-3} mm Hg] of the title compound (270a) (53 mg, 0.17 mmol) gave a yellow/brown liquid pyrolysate which, while still cold, was dissolved in deuteriochloroform. Inspection of the pyrolysate solution by ^1H NMR spectroscopy demonstrated that no sulphone-containing compounds were present, and that otherwise the pyrolysate was similar to that found on FVP of (270a) at 450°C. The only products identified were 3-(p-methoxyphenyl)isoxazole (476) (est. 20% yield) and p-methoxybenzonitrile (479) (est. 8%) [by comparison of ^1H NMR and IR spectra with those of commercially available material].

TLC (silica; ether) indicated the presence of three discrete product spots at R_f 0.42, 0.52 and 0.62. Preparative TLC (silica; ether) gave the separated three bands in low yield, but analysis by ^1H NMR spectroscopy of these indicated that a number of aromatic compounds were present in each, preventing further identification of the pyrolysis products.

5. FVP of (cis-2-transoid-2,3-cis-3-transoid-3,4-cis-4)-14-bridged-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]tetradec-12-ene 6,6-dioxide systems

a. FVP of cis-1,11-diphenyl-(cis-2-transoid-2,3-cis-3-transoid-3,4-cis-4)-12,13-benzo-14-oxa-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]tetradec-12-ene 6,6-dioxide (293)

i. At 500°C

FVP [160°C, 500°C, 4 x 10^{-3} mm Hg] of the title compound (293) (9 mg, 2.0 x 10^{-2} mmol) gave a mixture of yellow and green solids. This was dissolved in deuteriochloroform - analysis by ^{1}H NMR spectroscopy [confirmed by TLC (silica; ether) against authentic samples] demonstrated the presence of starting sulphone (293) (est. 42% recovered), 1,3-diphenylisobenzofuran (292) (est. 95% yield on consumed (293)) and cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (est. 82% yield). Examination of the pyrolysate by GLC (5% carbowax; 50°C) demonstrated that nine volatile products were present in low yield including benzene, toluene, ethyl benzene, o-xylene and styrene [from comparison of retention times with authentic samples].

ii. At 650°C

FVP [160°C, 650°C, 4 x 10^{-3} mm Hg] of the title compound (293) (6 mg, 1.4 x 10^{-2} mmol) gave a green/colourless solid pyrolysate. On addition of deuteriochloroform, a small quantity of colourless polymeric solid (ca 0.5 mg) was removed by filtration and the pyrolysate solution was found by ^{1}H NMR spectroscopy (calibrated by addition of methylene chloride (3.6 mg)) to contain 1,3-diphenylisobenzofuran (292) (est. 95% yield), cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (est. 12% yield) and miscellaneous volatile aromatic hydrocarbons

(ca 45% yield). GLC (5% carbowax; 50°C) indicated the volatile components to be almost identical in composition to those detailed in the earlier reported FVP of (293) at 500°C.

b. Vacuum pyrolysis of endo/exo-14-oxo-1,11,12,13-tetraphenyl-(cis-1-cisoid/transoid-1,2-cis-2-transoid-2,3-cis-3-transoid-3,4-cis-4)-6-thiapentacyclo[9.2.1.$0^{2,10}$.$0^{3,9}$.$0^{4,8}$]tetradec-12-ene 6,6-dioxide (295a)/(295b)

A 2:1 mixture of the title compounds (295a) and (295b) (41 mg, 7.4 x 10^{-2} mmol) was placed in a small 'cold-finger' sublimation apparatus and submitted to vacuum pyrolysis by heating to 205-210°C at a pressure of 5 x 10^{-3} mm Hg. The sample was observed to melt with evolution of gas which continued for a few minutes during which time the vacuum decreased to 2.5 x 10^{-2} mm Hg. After five minutes the melt crystallised and no further change in physical form was observed on continued heating at 210°C, 5 x 10^{-3} mm Hg for 1h. Upon cooling, the colourless crystalline pyrolysate was found to be pure 4,5,6,7-tetraphenyl-(cis-1-transoid-1,2-cis-2)-12-thiatricyclo-[8.3.0.$0^{2,9}$]trideca-3,5,7-triene 12,12-dioxide (490) (36 mg, 92%). Close examination of the thermal behaviour of the crystals revealed that a partial melting at 155-160°C took place, with a subsequent partial crystallisation observed upon slow increase of temperature; complete melting of the sample occurred at 237-242°C.

EA: $C_{36}H_{30}O_2S$ requires 82.1% C, 5.7% H; found 82.1% C, 5.9% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.21 (bd s; 6H), 3.78 (bd s; 2H), 6.10 (t, J = 2.0 Hz; 2H), 7.08 (s; 10H), 7.17-7.30 (m; 6H), 7.41-7.48 (m; 4H); ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 37.92 (CH), 44.23 (CH), 55.22 (CH_2), 126.66 (2xCH), 126.93 (CH), 127.30 (CH), 127.92 (2xCH), 128.15 (2xCH), 129.26 (CH), 129.81 (2xCH), 138.75 (Q),

139.07 (Q), 139.47 (Q), 144.84 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1597, 1490, 1464, 1381, 1297 (SO_2), 1239, 1156, 1138 (SO_2), 912, 878, 763, 732, 703; MS [EI] m/e (%): 526 (28; M^+), 462 (41), 408 (100), 382 (94), 230 (34), 178 (63), 167 (49), 153 (34), 91 (59), 78 (86).

G. Preparation, Diene Reactivity and FVP of cis- and trans-8-Thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxides (212), (235)

1. Diene reactivity of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212)

a. Dehydrogenation

To a solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (85 mg, 0.50 mmol) in dry benzene (5 ml) was added 10% palladium-on-charcoal (0.148 g) and the mixture heated under reflux under a dry nitrogen atmosphere for 15h, by which time TLC (silica; ether) monitoring indicated the absence of starting sulphone (212) (UV-active spot, R_f 0.51) and the presence of a single product spot (non-UV-active, R_f 0.59). The catalyst was filtered off, washed with benzene and the combined filtrate and washings reduced in vacuo to give a colourless crystalline residue (81 mg). Recrystallisation of this from chloroform/diisopropyl ether gave 3,4-benzo-1-thiacyclopent-3-ene 1,1-dioxide (110) (46 mg, 55%) as colourless rhombs, m.p. 149-150°C (lit.[202] m.p. 150-152°C), identical in all respects to a sample independently prepared (see p. 444).

b. Diels-Alder reactions

i. With dimethyl acetylenedicarboxylate

A solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (0.1537 g, 0.904 mmol) and dimethyl acetylenedicarboxylate (0.1464 g, 1.031 mmol) in A.R. benzene (5 ml) was heated under reflux for 56h. On cooling, the product solution was evaporated in vacuo to leave a light yellow oil which was triturated with ether. Filtration of the resultant mixture gave a colourless solid (0.1159 g) which was

recrystallised from methanol to afford dimethyl exo-4-thiatricyclo-[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (92.5 mg, 33%) as colourless crystals, m.p. 143-144.5°C.

EA: $C_{14}H_{16}O_6S$ requires 53.8% C, 5.2% H; found 53.6% C, 5.3% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.30-2.91 (m; 4H), 3.01-3.42 (m; 2H), 3.78 (s; 6H), 4.00-4.22 (m; 2H), 6.53 (dd, J = 4.3 Hz, 3.3 Hz; 2H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 37.92, 41.46, 52.27, 53.51, 133.94, 141.50 (Q), 165.13 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1733 and 1710 (CO), 1297 (SO_2), 1266, 1237, 1222, 1147 (SO_2), 1134, 1102, 1077, 912, 759; MS [EI] m/e (%): 312 (3; M^+), 281 (8), 194 (32), 164 (28), 163 (100), 77 (26), 54 (22).

ii. With maleic anhydride

A solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (0.984g, 5.79 mmol) and maleic anhydride (0.633g, 6.46 mmol) in dry benzene (20 ml) was heated under reflux for 20h with formation of a crystalline precipitate. On cooling, the crystals (0.908g) were filtered off and dried in vacuo; a further crop (52 mg) was realised on concentration of the benzene filtrate giving exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (493a) (0.960g, 62%) as colourless crystals, m.p. 297.5-298°C.

EA: $C_{12}H_{12}O_5S$ requires 53.7% C, 4.5% H; found 53.4% C, 4.6% H; ^{1}H NMR (CD_3SOCD_3; 250 MHz) δ [ppm]: 2.27 (dist dd, $J_{3a,3b}$ ($J_{5a,5b}$) = 9.5 Hz, $J_{2,3b}$ ($J_{5b,6}$) = 7.0 Hz; H_{3b}, H_{5b}), 2.57 (dist dd, $J_{2,3b}$ ($J_{5b,6}$) = 7.0 Hz, $J_{2,3a}$ ($J_{5a,6}$) = 4.0 Hz; H_2,H_6), 2.94 (bd s; H_1, H_7), 3.08 (dd, $J_{3a,3b}$ ($J_{5a,5b}$) = 9.5 Hz, $J_{2,3a}$ ($J_{5a,6}$) = 4.0 Hz; H_{3a}, H_{5a}), 3.29 (s; H_8,H_9), 6.20 (dd, $J_{1,11}$ ($J_{7,10}$) = 2.5 Hz, $J_{1,10}$ ($J_{7,11}$) = 1.8 Hz; H_{10}, H_{11}) - assignments of signals to protons, and coupling

constants, made on the basis of ^{1}H-2D COSY and 2D NOESY NMR analyses; ^{13}C NMR (CD_3SOCD_3; 25 MHz) δ [ppm]: 34.55, 35.62, 43.92, 52.37, 133.19, 173.07 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1847 and 1783 (CO), 1307 (SO_2), 1232, 1139 (SO_2), 1097, 1062, 952, 909, 783, 698; MS [EI] m/e (%): 268 (40; M^+), 196 (3), 175 (6), 170 (16), 150 (18), 131 (7), 122 (29), 105 (22), 91 (35), 78 (100).

iii. With butadiene sulphone

A solution of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (0.1955 g, 1.150 mmol) and butadiene sulphone (155.0 mg, 1.314 mmol) in AR benzene (10 ml) was heated under reflux for 56h. On cooling, the resultant solution was evaporated in vacuo to give a residue found by ^{1}H NMR spectroscopy to consist solely of the two starting materials (recovered quantitatively).

2. Preparation and diene reactivity of trans-8-thiabicyclo[4.3.0]-nona-2,4-diene 8,8-dioxide (235)

a. Preparation of trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235)

i. trans-5,6-Bis(hydroxymethyl)cyclohexa-1,3-diene (495)

A solution of trans-1,2-dihydrophthalic acid[100] (494) (0.560g, 3.33 mmol) in dry tetrahydrofuran (10 ml) was added dropwise, over a period of 30 min, to a stirred suspension of lithium aluminium hydride (0.360g, 9.47 mmol) in dry tetrahydrofuran (20 ml) under a dry nitrogen atmosphere. On completion of addition, the resultant grey/green mixture was heated under reflux with stirring for 3h, cooled, and the excess of lithium aluminium hydride destroyed by sequential addition of water (0.5 ml) in tetrahydrofuran (3.5 ml), 15% sodium hydroxide

solution (0.5 ml), and finally water (0.5 ml). The inorganic salts were filtered off, washed with tetrahydrofuran and then methylene chloride, and the combined filtrate and washings evaporated *in vacuo* to dryness. Dissolution of the residue in methylene chloride (20 ml) followed by drying over anhydrous magnesium sulphate and reduction *in vacuo* of the dried filtrate gave *trans*-5,6-bis(hydroxymethyl)cyclohexa-1,3-diene (495) (0.349g, 75%) as a light yellow oil.

^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.27-2.80 (bd hump; 4H), 3.46-3.79 (m; 4H), 5.48-5.75 (m; 2H), 5.82-6.08 (m; 2H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 38.43, 64.53, 124.31, 125.98; IR (neat film) $\nu_{max.}$ [cm^{-1}]: 3650-3000 (OH), 2925, 2872, 1459, 1413, 1367, 1202, 1025, 952, 696; MS [EI] m/e (%): 140 (7; M^+), 122 (22), 120 (27), 107 (25), 104 (18), 93 (72), 92 (87), 91 (90), 79 (100).

ii. *trans*-5,6-Bis(p-toluenesulphonyloxymethyl)cyclohexa-1,3-diene (227)

A solution of *trans*-5,6-bis(hydroxymethyl)cyclohexa-1,3-diene (495) (0.285g, 2.04 mmol) in pyridine (10 ml) was added dropwise, over a period of 50 min, to a stirred solution of *p*-toluene sulphonyl chloride (2.322g, 12.19 mmol) in pyridine (10 ml) at 0°C, with precipitation of a little colourless solid. After stirring at 0°C for a further 3h, the mixture was added to iced water (100 ml), the resultant mixture treated with 10% hydrochloric acid solution until just acidic and the precipitate present filtered off, washed well with water and dried *in vacuo* to give a colourless solid (0.611g). Recrystallisation from methylene chloride/isopropanol gave *trans*-5,6-bis(p-toluenesulphonyloxymethyl)-cyclohexa-1,3-diene (227) (0.470g, 52%) as colourless flakes, m.p. (decomp.) 101-101.5°C.

EA: $C_{22}H_{24}O_6S_2$ requires 58.9% C, 5.4% H; found 58.8% C, 5.4% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.39-2.78 (m; 8H), 3.75-3.98 (m; 4H), 5.28-5.57 (m; 2H), 5.79-6.02 (m; 2H), 7.33 and 7.74 (A_2B_2 pattern, J = 8.4 Hz; 8H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 21.44, 33.34, 68.41, 122.90, 125.64, 127.68 (2xCH), 129.74 (2xCH), 132.77 (Q), 144.73 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1596, 1357, 1189, 1166, 1097, 941, 837, 812, 699, 664; MS [EI] m/e (%): M^+ not apparent, 173 (22), 172 (100), 155 (27), 108 (43), 107 (84), 106 (36), 91 (96).

The ditosylate (227) was found to decompose to a black tar on exposure to atmosphere for several weeks.

iii. trans-8-Thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235)

The procedure described by Paquette *et al*[105] for the preparation of anhydrous sodium sulphide in hexamethylphosphoramide (HMPA) was followed. A stirred mixture of sodium sulphide nonahydrate (13.18g, 54.92 mmol) and HMPA (50 ml) was dehydrated by heating under reduced pressure (25 mm Hg) and distilling off a fraction (10 ml) until a stillhead temperature of 125°C had been attained. On cooling to room temperature, trans-5,6-bis(*p*-toluenesulphonyloxymethyl)cyclohexa-1,3-diene (227) (5.034g, 11.24 mmol) was added and the resultant light green mixture stirred for 23h by which time TLC (alumina; ether) determined that the ditosylate (227) (R_f 0.41) had been completely consumed with formation of a product spot, R_f 0.67. On addition of water (100 ml), the resultant aqueous solution was extracted with ether (4 x 200 ml), the combined extracts washed with water (3 x 150 ml), dried over anhydrous magnesium sulphate and the derived dried filtrate reduced *in vacuo* to give a residue of yellow oil (1.44g). This was Kugelrohr distilled at 70-80°C, 0.3 mm Hg to give a colourless oil

(1.01g), the ^{1}H and ^{13}C NMR spectra of which were in accord with a 3:1 mixture of trans-8-thiabicyclo[4.3.0]nona-2,4-diene (228) and benzyl methyl sulphide (as lit.[223] ^{1}H NMR spectrum).

A portion of the sulphide mixture (0.472g, 3.37 mmol) was dissolved in dry ether (10 ml) and stirred at 0°C during the dropwise addition, over one hour, of a solution of m-chloroperoxybenzoic acid (1.46g '85%' w/w = 1.24g, 7.19 mmol) in dry ether (30 ml). After stirring at room temperature for 44h, the product solution was washed with excess saturated sodium carbonate solution, dried over anhydrous magnesium sulphate and the resultant dried filtrate evaporated in vacuo to give a colourless solid (0.413g). By the use of preparative TLC (silica; ether), the major product (R_f 0.58) was separated from the minor product (R_f 0.48) [identified as benzyl methyl sulphone (226) by comparison with the ^{1}H NMR spectrum with an authentic sample - see p.444] to give trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235) (0.238g, 27% yield from ditosylate (227)), obtained as colourless needles, m.p. 129-132°C, on recrystallisation from methylene chloride/diisopropyl ether.

EA: $C_8H_{10}O_2S$ requires 56.4% C, 5.9% H; found 56.8% C, 6.0% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.72-3.41 (m; 6H), 5.75-6.17 (m; 4H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.85 (CH), 56.62 (CH_2), 126.29 (CH), 126.63 (CH); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1412, 1318, 1296 (SO_2), 1234, 1176, 1114 (SO_2), 1035, 897, 781, 683; MS [EI] m/e (%): 170 (15; M^+), 105 (35), 104 (23), 91 (100), 78 (20), 65 (22); UV (ether) $\lambda_{max.}$[nm]($\epsilon_{max.}$) : 258 (1275).

b. Diene reactivity of trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235) towards maleic anhydride

A solution of trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235) (56 mg, 0.33 mmol) and maleic anhydride (39 mg, 0.40 mmol) in dry benzene (3 ml) was heated under reflux for 45h. On cooling, the reaction solution was evaporated to dryness in vacuo and the residue triturated with dry ether/ dry methylene chloride. The colourless solid present was filtered off and dried in vacuo to constant weight (7 mg). This product appeared to be polymeric in nature since it could not be sublimed on application of heat up to a temperature of 250°C at 0.05 mm Hg. Evaporation of the trituration filtrate gave a colourless oil (82 mg), found by TLC (silica; ether) and ^{1}H NMR spectroscopy to contain solely equimolar amounts of the two starting materials.

3. FVP of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) and hydro/dehydro derivatives

a. FVP of cis-8-thiabicyclo[4.3.0]nonane 8,8-dioxide (308)

i. At 650°C

FVP [50°C, 650°C, 6 x 10^{-3} mm Hg] of the title compound (308) (36 mg, 0.21 mmol) gave a pyrolysate of colourless solid and oil, found to be pure starting sulphone (308) (33 mg, 92% recovered) by ^{1}H NMR analysis. Examination of the pyrolysate by GLC (10% PEGA; 60°C) confirmed the absence of volatile products.

ii. At 850°C

FVP [70°C, 850°C, 5 x 10^{-3} mm Hg] of the title compound (308) (28 mg, 0.16 mmol) gave a mixture of an unidentified polymeric

solid (2 mg) and a colourless oil. The latter was dissolved - whilst still cold - in deuteriochloroform and analysis by ^{1}H NMR spectroscopy (calibrated by addition of chloroform (7.0 mg)) and GLC (10% PEGA; 60°C) confirmed the presence of starting sulphone (308) (est. 3.6 mg, 13% recovered), octa-1,7-diene (est. 6.4 mg, 41% yield on consumed (308)) [identified by comparison with an authentic sample], benzene (est. 0.2 mg, 2%) and buta-1,3-diene (not quantified). In addition, two very minor (unidentified) volatile products were detected by GLC.

iii. At 925°C

FVP [75°C, 925°C, 5 x 10^{-3} mm Hg] of the title compound (308) (54 mg, 0.31 mmol) gave a pyrolysate of an unidentified polymeric solid (11 mg) and a colourless oil. The oil was dissolved, whilst still cold, in deuteriochloroform and analysed by ^{1}H NMR spectroscopy (calibrated by addition of chloroform (7.0 mg)) and GLC (10% PEGA; 60°C). These demonstrated the absence of starting sulphone (308) and presence of octa-1,7-diene (est. 6.8 mg, 20% yield), benzene (est. 0.7 mg, 3%) and increased quantities of buta-1,3-diene (not quantified) and the two unidentified volatile products detected on FVP of (308) at 850°C (described above).

b. FVP of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212)

i. At 625°C

FVP [105°C, 625°C, 5 x 10^{-3} mm Hg] of the title compound (212) (61.2 mg, 0.360 mmol) gave a colourless solid pyrolysate, found to be pure starting sulphone (212) (61 mg, quantitative recovery) following analysis by ^{1}H NMR spectroscopy and TLC (silica; ether).

ii. At 850°C

FVP [140°C, 850°C, 3 x 10^{-3} mm Hg] of the title compound (212) (44.0 mg, 0.259 mmol) gave a pyrolysate of yellow-coloured oil which was dissolved, while still cold, in deuteriochloroform. Analysis of the product solution by ^{1}H NMR spectroscopy and GLC (10% PEGA; 90°C) and comparison with standard solutions of the hydrocarbons present allowed identification and quantification of the following: starting sulphone (212) (est. 15% recovered), benzene (est. 50% yield on total starting sulphone (212)), toluene (est. 3%), ethylbenzene (est. 8%), o-xylene (est. 5%), styrene (est. 11%), other volatiles (2- not identified - est. 2%).

c. FVP of trans-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (235)

FVP [90°C, 650°C, 4 x 10^{-3} mm Hg] of the title compound (235) (3 mg, 0.02 mmol) gave a pyrolysate consisting of a yellow liquid. This was dissolved (while still very cold) in deuteriochloroform and analysed by ^{1}H NMR spectroscopy, GLC (5% carbowax; 50°C) and GC-MS. These confirmed the absence of starting sulphone (235) and the presence of o-xylene (est. 14% yield), benzocyclobutene (112) (est. 4%) and styrene (2%) following comparison of ^{1}H NMR spectra and GLC data with standard solutions of authentic samples of these hydrocarbons. The major product - which possessed the shortest retention time (t_R = 5.1 min) on GLC (5% carbowax; 50°C) analysis - was found to be of formula C_8H_{10} following analysis of the GC-MS data: GC-MS [EI] m/e (%): 106 (54; M^+), 105 (24), 91 (100), 79 (21), 78 (43), 77 (22), 65 (20), 51 (26), 39 (32), 27 (18). This product was tentatively assigned to an 85:15 equilibrium mixture of (Z,Z,Z)-cycloocta-1,3,5-triene (150) and bicyclo[4.2.0]octa-2,4-diene (206) [est. 65% yield] following the location of olefinic and saturated signals in the proton spectrum which

were in accord with those expected for this compound. However, this assignment remains unsubstantiated.

d. FVP of 8-thiabicyclo[4.3.0]nona-1,3-diene 8,8-dioxide (230)

i. At 850°C

FVP [130°C, 850°C, 7 x 10^{-3} mm Hg] of the title compound (230) (33.2 mg, 0.195 mmol) gave a mixture of colourless solid and yellow liquid. While still cold, this was dissolved in deuteriochloroform and analysed by ^{1}H NMR spectroscopy (calibrated with added chloroform (4.5 mg) for calculation of yields) and GLC (10% PEGA; 90°C). The pyrolysate was found to contain starting sulphone (230) (est. 52% recovered), benzene (est. 0.5% yield - calculated from total starting sulphone (230)), toluene (est. 7%), ethylbenzene (est. 1.5%), o-xylene (est. 1.5%), styrene (est. 21%) and two unidentified volatile products (est. 4%). The hydrocarbons were identified and quantified by GLC comparison with standard solutions of authentic samples.

ii. At 900°C

FVP [140°C, 900°C, 5 x 10^{-3} mm Hg] of the title compound (230) (39.0 mg, 0.229 mmol) gave a pyrolysate of a colourless solid and yellow oil. Dissolution of this, while still cold, in deuteriochloroform and analysis (as in (i) above) demonstrated the pyrolysate to consist of starting sulphone (230) (est. 17% recovered), benzene (est. 6% yield), toluene (est. 17%), ethylbenzene (est. 4.5%), o-xylene (est. 0.5%), styrene (est. 16%) and the two unidentified volatile products (est. 3.5%) found on FVP of (230) at 850°C.

iii. At 950°C

FVP [150°C, 950°C, 7 x 10^{-3} mm Hg] of the title compound (230) (38.3 mg, 0.225 mmol) gave a mixture of colourless solid and yellow oil, dissolved (while still cold) in deuteriochloroform and analysed as before (see (i) above). The pyrolysate was found to contain starting sulphone (230) (est. 2% recovered), benzene (est. 11% yield), toluene (est. 35%), ethylbenzene (est. 5%), o-xylene (est. 0.5%), styrene (est. 37%) and the two unidentified volatile products (est. 2%) found on FVP of (230) at 850°C.

e. FVP of 3,4-benzo-1-thiacyclopent-3-ene 1,1-dioxide (110)

i. At 500°C

FVP [70°C, 500°C, 6 x 10^{-3} mm Hg] of the title compound (110) (4 mg, 0.02 mmol) gave a pyrolysate consisting of a colourless liquid and solid which was dissolved, whilst still cold, in deuteriochloroform. Analysis of the product solution by ^{1}H NMR spectroscopy (yields calculated by addition of methylene chloride (3.25 mg)) and GLC (5% carbowax; 50°C) indicated the presence of starting sulphone (110) (est. 1.0 mg, 25% recovered) and benzocyclobutene (112) (est. 1.9 mg, quantitative yield on consumed (110)) [^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 3.18 (s; 4H), 6.97-7.22 (m; 4H)].

ii. At 850°C

FVP [80°C, 850°C, 5 x 10^{-3} mm Hg] of the title compound (110) (3 mg, 0.02 mmol) gave a colourless oil, dissolved in deuteriochloroform while still cold and analysed by ^{1}H NMR spectroscopy (yield estimated by addition of chloroform (3.25 mg)) and GLC (5% carbowax; 50°C) which determined that benzocyclobutene (112) (est. 1.7 mg, 92%) was the only compound present.

H. Preparation, Olefin Reactivity and FVP of 4-Thiatricyclo[5.2.2.$0^{2,6}$]-undec-8-ene/undeca-8,10-diene 4,4-dioxide Systems

1. Olefin reactivity of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a)

a. With 1,3-dipoles

i. With p-anisonitrile oxide (264)

α. Generated by base elimination of hydrogen chloride from p-anisohydroxamic chloride (269)

A solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (0.163g, 0.522 mmol) and p-anisohydroxamic chloride[228] (269) (0.292g, 1.57 mmol) in benzene (5 ml) was stirred at room temperature during the dropwise addition, over a period of 7h, of a solution of triethylamine (0.161g, 1.59 mmol) in benzene (9 ml). After stirring for 60h, the fine, light yellow precipitate which had formed was filtered off, washed well with benzene and then water, and dried in vacuo to give pure dimethyl 5-(p-methoxyphenyl)-3-oxa-10-thia-4-azatetracyclo[5.5.2.$0^{2,6}$.$0^{8,12}$]-tetradeca-4,13-diene-13,14-dicarboxylate 10,10-dioxide (510) (0.135g, 56%), m.p. (decomp.) 275.5-277°C on recrystallisation from benzene/acetone (70% recovery).

EA: $C_{22}H_{23}NO_8S$ requires 57.3% C, 5.0% H, 3.0% N; found 57.2% C, 5.2% H, 3.2% N; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.55-3.42 (cm; 8H), 3.48 (s; 3H), 3.80 (s; 3H), 3.83 (s; 3H), 4.18 (dd, J = 10.1 Hz, 2.6 Hz; 1H), 5.15 (dd, J = 10.1 Hz, 3.7 Hz; 1H), 6.91 and 7.50 (A_2B_2 pattern, J = 8.9 Hz; 4H); ^{13}C NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 31.89, 33.24, 35.95, 37.65, 46.73, 49.44, 49.94, 51.75,

52.17, 55.26, 77.87, 114.08 (2 x CH), 120.78, 128.51 (2 x CH), 137.40, 139.95, 156.20, 160.51, 164.53, 164.75; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1741 and 1717 (CO), 1612, 1517, 1308 (SO_2), 1281, 1254, 1210, 1138 (SO_2), 1097, 831; MS [EI] m/e (%): 461 (78; M^+), 430 (3), 402 (5), 374 (8), 343 (5), 315 (7), 255 (15), 175 (100), 163 (10), 160 (9), 147 (14), 132 (18), 78 (34), 77 (27).

Following evaporation of the benzene reaction filtrate to dryness, examination of the residual mixture by ^1H NMR spectroscopy demonstrated the presence of starting sulphone (492a) (est. 26 mg, 16% recovery).

β. Generated by thermal elimination of hydrogen chloride from p-anisohydroxamic chloride (269)

A solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (0.165g, 0.529 mmol) and p-anisohydroxamic chloride[228] (269) (0.198g, 1.07 mmol) in dry toluene (10 ml) was heated under reflux for 28h, by which time TLC (silica; ether) monitoring established the absence of starting sulphone (492a). On cooling, light brown needle crystals (25 mg) formed and these were removed by filtration; evaporation of the toluene filtrate in vacuo, followed by trituration of the residue with ether and filtration yielded a second crop of dimethyl 5-(p-methoxyphenyl)-3-oxa-10-thia-4-azatetracyclo[5.5.2.$0^{2,6}$.$0^{8,12}$]tetradeca-4,13-diene-13,14-dicarboxylate 10,10-dioxide (510) (total 51 mg, 21%), identical in all respects to that obtained in (α) above.

ii. With diazomethane (266)

α. Preparation of dimethyl 10-thia-3,4-diazatetracyclo[5.5.2.$0^{2,6}$.$0^{8,12}$]-tetradeca-3,13-diene-endo-cis-2,6-dicarboxylate 10,10-dioxide (511)

To a solution of diazomethane (266) (est. 0.63g, 15.0 mmol) in ether (80 ml) [prepared by the procedure described by Vogel[230]] was added dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (0.464g, 1.49 mmol) and the resultant mixture maintained at 0-3°C. After 12h, colourless flakes had formed; after seven days, TLC (silica; ether) indicated that starting sulphone (492a) was absent. The excess of diazomethane and ether was removed by evaporation in vacuo, the residue triturated with ether and the solid present filtered off and dried in vacuo to give dimethyl 10-thia-3,4-diazatetracyclo[5.5.2.$0^{2,6}$.$0^{8,12}$]tetradeca-3,13-diene-endo-cis-2,6-dicarboxylate 10,10-dioxide (511) (0.427g, 81%) as colourless flakes, m.p. (decomp.) 216-219°C.

EA: $C_{15}H_{18}N_2O_6S$ requires 50.8% C, 5.1% H, 7.9% N; found 50.6% C, 5.3% H, 8.1% N; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.30-3.54 (bd m; 6H), 3.56-3.97 (m; 8H), 4.43 and 5.03 (AB pattern: d, $J_{5a,5b}$ = 19.1 Hz; H_{5a},H_{5b}), 6.25 (t, J = 3.9 Hz; H_{13}, H_{14}); ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 32.11 (CH), 34.08 (CH), 38.12 (CH), 41.39 (CH), 52.27 (CH_2), 52.62 (CH_2), 52.77 (CH_3), 52.92 (CH_3), 55.04 (Q), 88.12 (CH_2), 103.35 (Q), 131.91 (CH), 134.29 (CH), 167.22 (Q), 171.20 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1726 (CO), 1574 (N=N), 1436, 1313, 1284, 1261, 1208, 1149, 1104, 961, 878; MS [EI] m/e (%): 355 (0.5; $(M+1)^+$), 326 (1), 295 (4), 281 (3), 262 (8), 235 (7), 208 (7), 193 (54), 176 (28), 163 (97), 149 (99), 148 (99), 143 (40), 133 (99), 128 (70), 118 (100), 105 (37), 91 (100).

β. Preparation of dimethyl 4-thiatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-endo-cis-8,10-dicarboxylate 4,4-dioxide (512)

A solution of dimethyl 10-thia-3,4-diazatetracyclo[5.5.2.$0^{2,6}$.$0^{8,12}$]tetradeca-3,13-diene-endo-cis-2,6-dicarboxylate 10,10-dioxide (511) (0.180g, 0.51 mmol) in acetonitrile (5 ml) was irradiated through quartz glassware using a 100W medium pressure mercury lamp. The course of the photolysis was monitored by ^{1}H NMR spectroscopy and found to be complete after five days. After filtering to remove a small quantity of solid, the filtrate was evaporated in vacuo to give a residue of colourless oil (0.161g) which crystallised on standing. Recrystallisation from methanol gave dimethyl 4-thiatetracyclo-[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-endo-cis-8,10-dicarboxylate 4,4-dioxide (512) (0.100g, 60%) as colourless cuboid crystals, m.p. 160.5-161°C.

EA: $C_{15}H_{18}O_6S$ requires 55.2% C, 5.6% H; found 55.0% C, 5.7% H; ^{1}H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 1.15 (AB pattern: d, $J_{9a,9b}$ = 5.6 Hz; H_{9b}) and 1.68 (AB pattern: d, $J_{9a,9b}$ = 5.6 Hz; H_{9a}), 2.50 (dd, $J_{3a,3b}$ ($J_{5a,5b}$) = 12.5 Hz, $J_{2,3b}$ ($J_{5b,6}$) = 10.5 Hz; H_{3b}, H_{5b}), 3.11 (dd, $J_{3a,3b}$ ($J_{5a,5b}$) = 12.5 Hz, $J_{2,3a}$ ($J_{5a,6}$) = 7.9 Hz; H_{3a}, H_{5a}), 3.25 (bd s; H_1, H_7), 3.32-3.45 (m; H_2, H_6), 3.68 (s; 6H), 6.07 (dd, J = 4.8 Hz, 3.5 Hz; H_{11}, H_{12})-assignments of signals to protons, and coupling constants, were made on the basis of ^{1}H selectively decoupled and ^{1}H NOE NMR spectra; ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 17.72, 31.05 (2 x Q), 34.98 (2 x C), 36.73 (2 x C), 52.35 (2 x C), 53.15 (2 x C), 131.11 (2 x C), 170.85 (2 x Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1734 and 1717 (CO), 1438, 1309 (SO_2), 1244, 1160 (SO_2), 1140, 1100, 796, 766; MS [EI] m/e (%): 326 (3; M^+), 295 (58), 294 (23), 262 (10), 235 (11), 230 (49), 208 (100), 203 (22), 202 (23), 193 (100), 176 (35), 163 (23), 149 (99), 143 (47), 91 (68).

b. Epoxidation

To a stirred solution of 30% 'w/v' hydrogen peroxide solution (1.50 ml, 13.2 mmol) in acetic acid (3.6 ml) at 60°C was added dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (0.292g, 0.936 mmol). After one day, the reaction solution was cooled with precipitation of a colourless solid; after stirring of the resultant mixture at room temperature for 2 days, the solid present was filtered off, washed with methylene chloride and dried in vacuo to give dimethyl 9-oxa-4-thiatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodec-11-ene-11,12-dicarboxylate 4,4-dioxide (515) (0.111g, 36%) as a colourless powder, m.p. 260-262°C.

EA: $C_{14}H_{16}O_7S$ requires 51.2% C, 4.9% H; found 51.0% C, 5.1% H; ^{1}H NMR (CD_3SOCD_3; 80 MHz) δ [ppm]: 3.13-3.33 (m; 6H), 3.45-3.64 (bd m; 2H), 3.67-3.80 (m; 8H); ^{13}C NMR and ^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 34.39 (CH), 36.24 (CH), 43.70 (CH_3), 49.92 (CH_2), 52.09 (CH), 134.82 (Q), 164.77 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1740 and 1713 (CO), 1306 (SO_2), 1268, 1253, 1237, 1222, 1141 (SO_2), 1103, 1072, 945, 913, 840; MS [EI] m/e (%): 328 (37; M^+), 297 (81), 268 (56), 237 (60), 203 (86), 171 (66), 161 (71), 145 (80), 117 (100), 91 (68).

Evaporation in vacuo of the acetic acid reaction filtrate gave a colourless semi-solid which was analysed by ^{1}H NMR spectroscopy and found not to contain further epoxide (515); appreciable quantities of starting sulphone (492a) (est. 88 mg, 30% recovered) were present.

c. Photochemical reactivity

i. Attempted intramolecular photocyclisation

α. Without a photosensitiser

A solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (23.2 mg, 0.074 mmol) in acetone (50 ml) was placed in a quartz flask and irradiated using a 100W medium pressure mercury lamp. Analysis by ^{1}H NMR spectroscopy of the photolysed solution after irradiation periods of 3h and 21h indicated that starting sulphone (492a) was present in unchanged quantity in both cases.

β. Using benzophenone as photosensitiser

A solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (34.2 mg, 0.110 mmol) and benzophenone (21.0 mg, 0.115 mmol) in dry acetone (50 ml) was irradiated through quartz using a 100W medium pressure mercury lamp for 32h. Evaporation of the product solution gave a yellow solid (86.2 mg), found by ^{1}H NMR analysis to contain starting sulphone (492a) (est. 20.5 mg, 60% recovered) and benzophenone (quantitative recovery). No photoproduct was apparent.

An identical photolysis to the above with the exception of the use of chloroform (rather than acetone) as solvent, gave similar results.

ii. With maleic anhydride

A solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (0.100g, 0.320 mmol) and maleic anhydride (35 mg, 0.357 mmol) in acetone (2.5 ml) was

irradiated (100W) through quartz glassware for 17h, by which time TLC (silica; ether) analysis determined that starting sulphone (492a) had been completely consumed, although no discrete product spots were apparent. Evaporation of the photolysis solution *in vacuo* gave a colourless solid (0.153g). Analysis of this by ^{1}H and ^{13}C DEPT NMR, and by infrared spectroscopy indicated this to be a copolymer of the two starting materials [no olefinic signals were observed in the proton spectrum]. This assignment was reinforced by a lack of sublimation of the product on slow heating up to 250°C at 0.4 mm Hg.

d. Hydrogenation

i. Preparation of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene-8,9-dicarboxylate 4,4-dioxide (517)

A suspension of 10% palladium-on-charcoal (28 mg) in a solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (0.183g, 0.587 mmol) in methanol (15 ml) was vigorously agitated under one atmosphere pressure of hydrogen for two hours, by which time uptake of hydrogen had almost ceased. The catalyst was filtered off and the filtrate evaporated under reduced pressure to give a light yellow solid (0.183g). Analysis of this by ^{1}H NMR spectroscopy indicated the absence of starting olefin (492a); TLC (silica; 4:1 ether/methanol) analysis indicated the presence of two product spots, R_f 0.65 (UV active) and 0.59. The higher R_f component was isolated by MPLC (silica; pet.-ether (b.p. 40-60°C) → ether → 95:5 ether/methanol) of the mixture followed by recrystallisation from methanol of the fractions containing the higher R_f product, giving dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene-8,9-dicarboxylate 4,4-dioxide (517) (53 mg, 29%) as colourless flakes, m.p. 199-201°C.

EA: $C_{14}H_{18}O_6S$ requires 53.5% C, 5.8% H; found 53.5% C, 5.5% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.17-1.98 (m; 4H), 2.36-3.30 (m; 8H), 3.77 (s; 6H); ^{13}C NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 17.96, 33.86, 34.03, 50.51, 52.14, 140.98 (Q), 165.52 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1732 and 1712 (CO), 1631, 1453, 1290 (SO_2), 1231, 1167, 1138 (SO_2), 1303, 1088, 902; MS [EI] m/e (%): 314 (3; M^+), 283 (100), 250 (14), 218 (47), 196 (56), 190 (94), 165 (53), 164 (72), 163 (78), 141 (13), 105 (18).

Evaporation of the combined product-containing fractions from MPLC and the recrystallisation filtrate, and analysis by ^{1}H and ^{13}C NMR spectroscopy identified the presence of further olefin (517) (est. 35 mg; 88 mg total, 48% yield from (492a)) together with the two fully saturated products (described in more detail in (ii) below), dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undecane-exo/endo-cis-8,9-dicarboxylate 4,4-dioxide (525) (est. 20 mg, 11% yield)/(524) (est. 45 mg, 24% yield).

ii. Preparation of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undecane-exo/endo-cis-8,9-dicarboxylate 4,4-dioxide (525)/(524)

A suspension of 10% palladium-on-charcoal (64 mg) in a solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a) (0.198g, 0.635 mmol) in 'superdry' ethanol (15 ml) was vigorously stirred under a pressure of one atmosphere of hydrogen for six hours, by which time uptake of hydrogen had almost ceased. TLC (silica; 4:1 ether/methanol) analysis indicated the absence of starting sulphone (492a) or olefin (517) (see (i) above) [both R_f 0.65] and the presence of a product spot, R_f 0.59. The catalyst was filtered off, washed with ethanol and the combined

filtrates evaporated in vacuo to give a 1:2 mixture of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undecane-exo/endo-cis-8,9-dicarboxylate 4,4-dioxide (525)/(524) (0.178 g, 89% combined) as evidenced by ^{1}H and ^{13}C NMR spectroscopic analyses.

The presence of the exo-cis isomer (525) was confirmed by enhancement of the ^{13}C NMR signals for the minor component upon addition of authentic material, prepared by an alternative route (see p.594); the major component was assigned endo-cis stereochemistry (524) by analogy of the NMR spectral properties and formation pathway to those of the exo-cis isomer (525). Since the two isomers could not be resolved by TLC using a variety of different solvent systems (thus preventing separation by column chromatography), nor separated by means of preferential crystallisation, the major product (524) could not be fully characterised [(524):- ^{1}H NMR spectrum similar (not distinguishable) to that of (525) (see p.595); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 19.08 (CH_2), 29.12 (CH), 30.36 (CH), 43.71 (CH), 50.91 (CH_2), 51.55 (CH_3)].

2. Preparation and olefin reactivity of dimethyl exo-4-thiatricyclo-[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506)

a. Preparation of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506)

A suspension of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (493a) (0.395g, 1.47 mmol) in AR grade methanol (15 ml) containing concentrated sulphuric acid (45 mg) was heated under reflux. After three hours, a solution had formed; after 7.5h, the product solution was cooled with precipitation of colourless flakes which were filtered off and dried in vacuo. A

second crop (72 mg) of pure product was obtained by concentration of the methanol filtrate to give dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]-undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506) (0.419g, 91%) as colourless flakes, m.p. 182-183°C, on recrystallisation from methanol.

EA: $C_{14}H_{18}O_6S$ requires 53.5% C, 5.8% H; found 53.6% C, 6.0% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 2.42-3.20 (m; 10H), 3.60 (s; 6H), 6.42 (dd, J = 4.7 Hz, 3.0 Hz; 2H); ^{13}C NMR ($CDCl_3$; 25 MHz) δ [ppm]: 35.68, 37.19, 46.57, 51.70, 52.57, 132.15, 171.84 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1731 (CO), 1436, 1367, 1330, 1307, 1286, 1234, 1194, 1141, 1097, 1046, 898, 734, 721; MS [EI] m/e (%): 314 (28; M^+), 283 (41), 255 (12), 223 (25), 170 (38), 137 (46), 105 (88), 93 (63), 91 (100), 78 (95), 59 (75).

b. Olefin reactivity of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]-undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506)

i. With 1,3-dipoles

α. With p-anisonitrile oxide (264)

A mixture of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506) (82 mg, 0.26 mmol) and p-anisohydroxamic chloride[228] (269) (0.123 g, 0.66 mmol) in dry toluene (10 ml) was heated under reflux, forming a solution after a few minutes. After 52h, the reaction solution was cooled with formation of colourless needle crystals. These were filtered off and dried to give starting sulphone (506) (72 mg, 88% recovered), as demonstrated by identical melting point, ^{1}H NMR and IR spectral data. Evaporation of the toluene filtrate in vacuo gave a residue found by

^{1}H NMR analysis to contain further starting sulphone (506), p-aniso-hydroxamic chloride (269) [and derived decomposition products], but no sulphone-containing products.

β. With diazomethane (266)

To a solution of dimethyl exo-4-thiatricyclo[5.2.2.0^{2,6}]-undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506) (0.252g, 0.803 mmol) in dry methanol (60 ml) was added a solution of diazomethane (266) (est. 0.334g, 7.95 mmol) in dry ether[230] (20 ml) and the resultant solution maintained at 0-3°C. Slow formation of colourless crystals occurred over a period of a few days; after 30 days, TLC (silica; ether) monitoring still indicated the presence of starting sulphone (506) in the yellow (ie diazomethane-containing) reaction solution. At this time, the mixture was reduced to small volume and the colourless flake crystals present filtered off and dried to give pure starting sulphone (506) (0.115 g), as identified by comparison of melting point, ^{1}H NMR and IR spectral data with authentic material. Evaporation of the filtrate to dryness gave further starting sulphone (506) (total 0.222g, 88% recovered), as shown by ^{1}H NMR analysis of the residue. No product was observed.

A repeat reaction involving the use of a 1:1:2 (by volume) mixture of dry ether, 'superdry' ethanol, and dry methylene chlorides as solvent - otherwise identical to the above reaction - gave parallel results.

ii. Epoxidation

α. Using peracetic acid

A solution of dimethyl exo-4-thiatricyclo[5.2.2.0^{2,6}]undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506) (0.3320g, 1.057 mmol)

in acetic acid (4.20 ml) containing 30% 'w/v' hydrogen peroxide solution (0.84 ml, 7.41 mmol) was stirred at 50-55°C. After 63h, precipitation of a colourless solid appeared complete and on cooling this was filtered off and dried *in vacuo*; evaporation of the filtrate to dryness *in vacuo* gave a second crop (0.105g) of *exo*-4-thiatricyclo-[5.2.2.$0^{2,6}$]undec-10-ene-*exo*-*cis*-8,9-dicarboxylic acid 4,4-dioxide (527) (total 0.271g, 90%) found to be identical in terms of melting behaviour and ^{1}H, ^{13}C NMR and IR spectral characteristics to an independently prepared sample (see p.596). A repeat experiment gave identical results.

β. Using m-chloroperoxybenzoic acid

A solution of dimethyl *exo*-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-*exo*-*cis*-8,9-dicarboxylate 4,4-dioxide (506) (40 mg, 0.13 mmol) and *m*-chloroperoxybenzoic acid (39 mg '85%' w/w = 33 mg, 0.19 mmol) in ethyl acetate (1.5 ml) was heated under reflux for 8h. On cooling, the yellow reaction mixture was evaporated to dryness *in vacuo* to give a slightly yellow crystalline residue. Analysis by ^{1}H NMR spectroscopy indicated that the only sulphone-containing compound in this was the starting material (506) (quantitative recovery), present as a mixture with *m*-chlorobenzoic and *m*-chloroperoxybenzoic acids.

iii. Photolysis with maleic anhydride

A solution of dimethyl *exo*-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-*exo*-*cis*-8,9-dicarboxylate 4,4-dioxide (506) (27 mg, 0.09 mmol) and maleic anhydride (12 mg, 0.12 mmol) in acetone (0.5 ml), contained in a quartz NMR tube, was irradiated using a 100W medium pressure mercury lamp and the course of the photolysis monitored by inspection of the unsaturated region of the proton spectrum. After 6h, ^{1}H NMR

analysis indicated the concentration of the sulphone (506) to be unchanged, though no maleic anhydride remained. Further maleic anhydride (12 mg, 0.12 mmol) was added and irradiation resumed: again, the added maleic anhydride was consumed after 14h with no observed change in the sulphone (506) concentration. A final addition of maleic anhydride (20 mg, 0.20 mmol) to the photolysis solution was consumed after irradiation for a further 20h (total irradiation period of 40h) with the starting sulphone (506) present in unchanged quantity from that at the initiation of the photolysis. A small quantity of colourless crystals (3 mg, 7%) present in the final photolysate was isolated by filtration and found to be identical (with respect to melting behaviour, infrared and mass spectral determinations) to an authentic sample of (cis-1-transoid-1,2-cis-2)-cyclobutane-1,2,3,4-tetracarboxylic dianhydride, m.p. (decomp.)>300°C, prepared in 21% yield by irradiation of a 0.59M solution of maleic anhydride in acetone under the above conditions for 7.5h[108].

iv. Hydrogenation

A suspension of 10% palladium-on-charcoal (27 mg) in a solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506) (95 mg, 0.30 mmol) in methanol (25 ml) was vigorously agitated under one atmosphere pressure of hydrogen until gas uptake had ceased (4h). TLC (silica; 4:1 ether/methanol) established the absence of starting sulphone (506) (R_f 0.51) and the presence of a single product spot, R_f 0.59. Therefore, the catalyst was filtered off and washed with methanol, and the combined filtrate and washings evaporated under reduced pressure, the residue treated with chloroform, the resultant mixture filtered and the filtrate reduced in vacuo to give pure dimethyl exo-4-thiatricyclo-

[5.2.2.$0^{2,6}$]undecane-exo-cis-8,9-dicarboxylate 4,4-dioxide (525) (87 mg, 91%) as a colourless solid. Recrystallisation from methanol gave fine colourless needles, m.p. 189-192°C (51% recovery).

EA: $C_{14}H_{20}O_6S$ requires 53.2% C, 6.4% H; found 53.4% C, 6.1% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.51 and 1.83 (bd A_2B_2 pattern: d, $J_{10a,10b}$ ($J_{11a,11b}$) = 12 Hz; H_{10a}, H_{10b}, H_{11a}, H_{11b}), 2.08 (bd s; 2H), 2.52-2.85 (m; 2H), 2.91-3.14 (m; 6H), 3.66 (s; 6H); ^{13}C NMR and ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 15.04 (CH_2), 29.32 (CH), 35.17 (CH), 44.16 (CH), 50.81 (CH_2), 51.62 (CH_3), 172.45 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1742 (CO), 1426, 1374, 1317 (SO_2), 1297, 1235, 1197 (SO_2), 1141, 1111, 1078, 1026, 924, 887; MS [EI] m/e (%): 316 (7; M^+), 285 (43), 284 (61), 256 (19), 252 (14), 224 (20), 197 (15), 191 (16), 170 (17), 146 (77), 145 (80), 131 (28), 114 (98), 113 (100), 105 (50), 91 (86), 79 (82).

v. Bromination

A solution of dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506) (80 mg, 0.25 mmol) in dry methylene chloride (2 ml) at 0°C was stirred during the dropwise addition of a solution of bromine (53 mg, 0.33 mmol) in dry methylene chloride (1 ml). Initially, only a few drops of bromine solution was added and since no decolourisation of this was observed after 15 min at 0°C, the remainder was added over a two min period. Thereafter, the red solution was heated under reflux for 48h with no change in appearance noted; TLC (silica; ether) monitoring indicated that only starting sulphone (506) was present throughout. Evaporation of the reaction solution to dryness gave a colourless solid (80 mg), found by ^{1}H NMR analysis to be pure starting sulphone (506), recovered quantitatively.

3. Preparation and olefin reactivity (towards bromine) of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (508)

a. Preparation of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (508)

i. Via exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (527)

α. exo-4-Thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (527)

A suspension of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (493a) (0.960g, 3.58 mmol) in water (25 ml) was heated under reflux for 2.5h. On cooling, the mixture was evaporated in vacuo to dryness giving exo-4-thiatricyclo-[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (527) (1.023g, 100%) as a colourless crystalline solid. The crystals were found to decompose (by loss of water) on heating to 235°C, giving the anhydride starting material (493a), m.p. 297-298°C.

EA: $C_{12}H_{14}O_6S$ requires 50.3% C, 4.9% H; found 50.2% C, 5.2% H; ^{1}H NMR (CD_3SOCD_3; 25 MHz) δ [ppm]: 2.27-3.56 (m; 10H), 6.26 (dd, J = 4.4 Hz, 3.2 Hz; 2H), 10.5-13.0 (v bd hump; 2H); ^{13}C NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 35.79, 36.98, 46.32, 52.86, 132.11, 173.29 (Q); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 3450-2400 (OH), 1728 (CO), 1405, 1292 (SO_2), 1281, 1237, 1221, 1146 (SO_2), 1107, 908, 880, 666; MS [EI] m/e (%): 286 (1; M^+), 268 (45), 196 (4), 175 (7), 170 (18), 150 (22), 122 (39), 105 (27), 91 (33), 78 (100), 65 (11), 54 (17).

β. Attempted preparation of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undecane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (532)

A suspension of 10% palladium-on-charcoal (85 mg) in a solution of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (527) (1.023g, 3.58 mmol) in acetic acid (200 ml) was vigorously agitated under one atmosphere pressure of hydrogen for 3h, by which time uptake of hydrogen had become very slow. The catalyst was filtered off, washed with acetic acid and the combined filtrate and washings evaporated in vacuo (40°C, 0.5 mm Hg) to leave a colourless crystalline residue. This was washed with ether and dried in vacuo to give pure exo-4-thiatricyclo[5.2.2.$0^{2,6}$]-undec-10-ene-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (493a) (0.795g, 83%) as evidenced by identical ^{1}H NMR and IR spectral comparisons with an authentic sample.

ii. Via exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undecane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (531)

α. exo-4-Thiatricyclo[5.2.2.$0^{2,6}$]undecane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (532)

A suspension of platinum oxide (Adam's catalyst) (0.157g) in a solution of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (493a) (0.760g, 2.84 mmol) in acetic acid (200 ml) was vigorously stirred under one atmosphere pressure of hydrogen for 5h, at which point uptake of hydrogen had almost ceased. The catalyst was filtered off, washed with acetic acid and the combined filtrate and washings evaporated in vacuo to give a colourless crystalline solid. After washing with ether and drying in vacuo, a mixture of starting olefin (493a) (est. 0.113g,

15% recovered) and exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undecane-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (531) (est. 0.643g, 84%) was obtained as a colourless solid (0.756g), as shown by ^{1}H NMR and IR analyses.

A stirred suspension of this mixture (0.740g) in water (25 ml) was heated under reflux for 1h giving a colourless solution. On cooling, colourless crystals (0.622g) were formed and these were filtered off and dried in vacuo; a second crop (identical in composition) was obtained by in vacuo evaporation of the filtrate to dryness followed by trituration with ether and drying in vacuo of the filtered solid to give a mixture of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (527) (est. 0.114g, 14% from (493a)) and exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undecane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (532) (est. 0.649g, 81% from (493a)) as a colourless solid, m.p. 210-220°C. The ratio of the two products was unchanged after recrystallisation from water, the minor component being identified by comparison of ^{1}H and ^{13}C NMR spectra with those of an authentic sample (p.596).

EA: 15:85 mixture of (527) ($C_{12}H_{14}O_6S$) and (532) ($C_{12}H_{16}O_6S$) requires 50.0% C, 5.5% H; found 50.1% C, 5.3% H; ^{1}H NMR (CD_3SOCD_3; 80 MHz) δ [ppm]: 1.57 (bd s; 2H), 1.88 (bd s; 2H), 2.28-3.49 (m; 10H), 11.20-12.50 (v bd hump; 2H) [(532) only]; ^{13}C DEPT NMR (CD_3SOCD_3; 50.3 MHz) δ [ppm]: 14.76 (CH_2), 28.91 (CH), 34.48 (CH), 43.55 (CH), 50.44 (CH_2) [(532) only]; IR (nujol) $\nu_{max.}$ [cm^{-1}]: 3500-2600 (OH), 1735 (CO), 1404, 1305, 1289 (SO_2), 1236, 1217, 1142 (SO_2), 1106, 853, 753; MS [EI] m/e (%): M^+ not apparent, 270 (12; $(M-H_2O)^+$), 268 (5), 224 (6), 198 (13), 118 (6), 105 (12), 91 (23), 80 (100), 78 (51), 65 (8), 55 (7).

β. exo-4-Thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide (508)

To oxygen saturated (by ebullition for 30 min) dry pyridine (20 ml) maintained at 67°C was added an 85:15 mixture of exo-4-thiatricyclo[5.2.2.0^{2,6}]undecane-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (532) and exo-4-thiatricyclo[5.2.2.0^{2,6}]undec-10-ene-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (527) (0.727g, 2.15 mmol and 0.38 mmol respectively) together with vacuum-dried lead tetraacetate (1.680g, 3.79 mmol). The resultant red mixture was stirred intermittently with evolution of gas observed after 2 min, this ceasing some 3 min later. At this time, the resultant brown solution was added to 12% nitric acid solution (240 ml) and the solution thus obtained extracted with methylene chloride (5 x 60 ml), the extracts combined, washed with 80% saturated sodium hydrogen carbonate solution (2 x 120 ml) followed by saturated sodium chloride solution (120 ml) and dried over anhydrous magnesium sulphate. Evaporation of the resultant dried filtrate in vacuo gave a light yellow semi-crystalline residue (0.293g) which was recrystallised from ethanol to give exo-4-thiatricyclo[5.2.2.0^{2,6}]undec-8-ene 4,4-dioxide (508) (95 mg, 22% from available (532)) as colourless fingers, m.p. 111-113°C. An equimolar mixture of this product and the endo isomer[33] (329) (m.p. 112-113°C) gave a mixed melting point of 77-84°C.

EA: $C_{10}H_{14}O_2S$ requires 60.6% C, 7.1% H; found 60.7% C, 6.9% H; ^{1}H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.21 and 1.73 (A_2B_2 pattern: d, $J_{10a,10b}$ ($J_{11a,11b}$) = 9.7 Hz; H_{10a}, H_{10b}, H_{11a}, H_{11b}), 2.35-2.57 (m; 4H), 2.91-3.10 (m; 4H), 6.37 (dd, J = 4.6 Hz, 2.9 Hz; H_8,H_9); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 18.11 (CH_2), 30.98 (CH), 34.01 (CH), 50.84 (CH_2), 134.39 (CH); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1408, 1300 (SO_2), 1289, 1233, 1169, 1136 (SO_2), 1104, 888, 837, 761, 742, 727;

MS [EI] m/e (%): 198 (22; M^+), 170 (4), 133 (7), 132 (11), 105 (13), 91 (30), 80 (100), 79 (52), 78 (57), 77 (28).

Evaporation of the recrystallisation filtrate gave a light yellow oil (0.195g), found by ^1H NMR and TLC (silica; ether) analyses to contain minor quantities of olefin (508) and 4-thiatricyclo[5.2.2.$0^{2,6}$]-undeca-8,10-diene 4,4-dioxide (507) [for preparation of an authentic sample of (507) see p.602], R_f 0.53 and 0.49 respectively.

b. Bromination of exo- and endo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (508), (329)

i. exo-4-Thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (508)

A solution of exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (508) (20 mg, 0.10 mmol) in dry methylene chloride (2 ml) was stirred at -78°C during the addition, via syringe over a period of one min, of a solution of bromine in methylene chloride (0.80 ml 0.188M = 24 mg, 0.15 mmol). The added bromine solution was quickly decolourised until excess had been added. After stirring at -78°C for 30 min, the red reaction solution was warmed to room temperature over a 30 min period and stirred for a further 45 min. Evaporation of the solution to dryness in vacuo gave a light yellow oil (40 mg), found by TLC (silica; ether) to be devoid of starting sulphone (508) and to exhibit a single product spot, R_f 0.49. Crystallisation of the crude product from chloroform (cooled to -20°C) gave trans-8,9-dibromo-exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undecane 4,4-dioxide (533) (26 mg, 72%) as colourless rhombs, m.p. 192-195°C.

EA: $C_{10}H_{14}Br_2O_2S$ requires 33.5% C, 3.9% H; found 33.7% C, 3.9% H; ^1H NMR ($CDCl_3$; 80 MHz) δ [ppm]: 1.68-2.14 (m; 6H), 2.85-3.26

(m; 6H), 4.35-4.60 (m; 2H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 13.50 (CH_2), 19.56 (CH_2), 28.87 (CH), 34.89 (CH), 36.90 (CH), 37.27 (CH), 50.37 (CH_2), 50.90 (CH_2), 58.35 (CH), 58.47 (CH); IR (nujol) $\nu_{max.}$[cm^{-1}]: 1298, 1291 (SO_2), 1257, 1233, 1222, 1173, 1160, 1153 (SO_2), 1101, 954, 777, 760, 658; MS [EI] m/e (%): 358 (4; $^{79,81}M^+$), 356 (9), 354 (4), 279 (45), 277 (45), 213 (10), 211 (10), 198 (13), 197 (100), 133 (38), 131 (42), 105 (44), 91 (78), 80 (42), 79 (76), 77 (47).

ii. endo-4-Thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (329)

A solution of endo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide[33] (329) (0.147g, 0.74 mmol) in chloroform (15 ml) was stirred at 0°C and a few drops of a solution of bromine (0.143g, 0.89 mmol) in chloroform (5 ml) added. No decolourisation was observed after 15 min, and the remainder of the bromine solution was added with the reaction solution then being heated under reflux for 1.5h. The resultant partially-decolourised solution was cooled and evaporated in vacuo to dryness to leave a residue of orange solid (0.216g), found on ^{1}H NMR and TLC (silica; ether) analyses to contain only starting olefin (329) (R_f 0.53).

This material was dissolved in a solution of bromine (0.221g, 1.38 mmol) in chloroform (20 ml) and the whole heated under reflux for 22.5h. Evaporation of solvent and the excess of bromine in vacuo gave an orange-coloured semi-crystalline residue (0.374g). Analysis of this by ^{1}H NMR spectroscopy and TLC (silica; ether) established the absence of starting olefin (329) and the presence of a complex array of brominated products which gave broad bands on TLC at R_f 0.66, 0.49 and 0.43. These three bands were separated by a combination

of flash chromatography and preparative TLC, and each was found to consist of several brominated (both saturated and olefinically unsaturated) products - none of which was identified - following analysis by ^{1}H and ^{13}C NMR spectroscopy.

4. Preparation and olefin reactivity of 4-thiatricyclo[5.2.2.$0^{2,6}$]-undeca-8,10-diene 4,4-dioxide (507)

a. Preparation of 4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene 4,4-dioxide (507)

To oxygen-saturated (by ebullition for 15 min) dry pyridine (100 ml) maintained at 67°C was added exo-4-thiatricyclo-[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic acid 4,4-dioxide (527) (2.50g, 8.74 mmol) and vacuum-dried lead tetraacetate (7.74g, 17.47 mmol). The resultant mixture was stirred intermittently and after 7 min slow evolution of gas was observed with this ceasing a further 13 min later. The resultant orange solution was added to 12% nitric acid solution (900 ml) and the aqueous solution formed was extracted with methylene chloride (5 x 200 ml), the extracts combined, washed with 80% saturated sodium hydrogen carbonate solution (500 ml), then saturated sodium chloride solution (500 ml), and dried over anhydrous magnesium sulphate. Evaporation of the dried filtrate gave a yellow semi-crystalline residue (1.10g) which demonstrated a major product spot (R_f 0.60) together with four minor components at lower R_f on TLC (silica; ether) analysis. The major product was isolated in pure form following separation by MPLC [silica; pet.-ether (b.p. 40-60°C) ⟶ ether] to give 4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene 4,4-dioxide (507) (0.488g, 28%) as colourless flakes, m.p. 147-150°C, on recrystallisation from methylene chloride/diisopropyl ether.

EA: $C_{10}H_{12}O_2S$ requires 61.2% C, 6.2% H; found 61.0% C, 6.0% H; ^1H NMR ($CDCl_3$; 200 MHz) δ [ppm]: 2.38-2.52 (m; 4H), 3.06-3.17 (sym m; 2H), 3.61 - 3.69 (sym m; 2H), 6.38-6.45 (cm; 4H); ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 38.12 (CH), 39.50 (CH), 54.09 (CH_2), 134.30 (CH), 134.61 (CH); IR (nujol) $\nu_{max.}$ [cm^{-1}]: 1362, 1330, 1304 (SO_2), 1259, 1221, 1143 (SO_2), 1100, 901, 863, 762, 638; MS [EI] m/e (%): 196 (14; M^+), 170 (1), 131 (8), 129 (5), 128 (4), 117 (15), 115 (15), 104 (11), 91 (27), 78 (100).

b. Olefin reactivity of 4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene 4,4-dioxide (507)

i. Attempted intramolecular photocyclisation

A solution of 4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene 4,4-dioxide (507) (31 mg, 0.16 mmol) in deuteriochloroform (2 ml) was irradiated through quartz glassware, using a 400W medium pressure mercury lamp, for 11.5h. The resultant dark-coloured solution was examined by ^1H and ^{13}C NMR spectroscopy. Only a little starting diene (507) (est. 3.0 mg, 10% recovered) was present, with the proton spectrum displaying predominantly (broad) saturated resonances. No discrete product was observed on analysis of the photolysis solution by TLC (silica; ether) and ^{13}C NMR spectroscopy; evaporation of the solution gave a light brown semi-crystalline residue (86 mg) and this appeared, on the basis of the above analyses, to be a polymeric material incorporating the solvent.

A repeat photolysis - identical to the above except for the use of a Vycor filter - gave similar results. A third photolysis, identical to the above except for the use of pyrex rather than quartz glassware, gave recovered starting diene in quantitative yield after irradiation for 70h.

ii. Bromination

A solution of 4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene 4,4-dioxide (507) (78 mg, 0.40 mmol) in chloroform (3 ml) was stirred at -60°C during the addition, via syringe over a 5 min period, of a solution of bromine in chloroform (0.22 ml 1.52M = 54 mg, 0.33 mmol). No decolourisation of the added bromine occurred and so the solution was allowed to warm to room temperature over a 2h period, and stirred at room temperature for 4.5 days. The resultant, almost colourless, solution was evaporated in vacuo to give a light orange crystalline residue (0.118 g) which was recrystallised from ethanol to give endo-9-exo-10-dibromo-4-thiatetracyclo[5.2.2.$0^{2,6}$.$0^{8,11}$]undecane 4,4-dioxide (538) (39 mg, 33%) as colourless flakes, m.p. 190-193°C.

EA: $C_{10}H_{12}Br_2O_2S$ requires 33.7% C, 3.4% H; found 33.8% C, 3.4% H; ^{1}H NMR ($CDCl_3$; 360 MHz) δ [ppm]: 1.39 (td, $J_{7,8} = J_{7,11} =$ 7.6 Hz, $J_{6,7} = 2.6$ Hz; H_7), 2.09 (overlap. dd, $J_{7,11} = 7.6$ Hz, $J_{8,11} =$ 5.5 Hz; H_{11}), 2.20 (overlap. ddd, $J_{7,8} = 7.6$ Hz, $J_{8,11} = 5.5$ Hz, $J_{8,9} = 3.6$ Hz; H_8), 2.36 (overlap. dd, $J_{1,9} = 5.2$ Hz, $J_{1,2} =$ 3.3 Hz; H_1), 2.83 (ddd, $J_{5a,5b} = 13.2$ Hz, $J_{5b,6} = 10.7$ Hz, $J_{3b,5b} =$ 0.7 Hz; H_{5b}), 2.94 (ddd, $J_{3a,3b} = 14.2$ Hz, $J_{2,3b} = 10.0$ Hz, $J_{3b,5b} =$ 0.7 Hz; H_{3b}), 3.09-3.18 [cm comprising 3.13 (ddd, $J_{3a,3b} = 14.2$ Hz, $J_{2,3a} = 10.0$ Hz, $J_{3a,5a} = 2.3$ Hz; H_{3a}) and 3.13 (dddd, $J_{5b,6} = 10.7$ Hz, $J_{2,6} = 10.0$ Hz, $J_{5a,6} = 8.0$ Hz, $J_{6,7} = 2.6$ Hz; H_6)], 3.27 (ddd, $J_{5a,5b} =$ 13.2 Hz, $J_{5a,6} = 8.0$ Hz, $J_{3a,5a} = 2.3$ Hz; H_{5a}), 3.44 (qd, $J_{2,3a} =$ $J_{2,3b} = J_{2,6} = 10.0$ Hz, $J_{1,2} = 3.3$ Hz; H_2), 4.54 (s; H_{10}), 5.03 (dd, $J_{1,9} = 5.2$ Hz, $J_{8,9} = 3.6$ Hz; H_9) - assignments of signals to protons, and of coupling constants, were made by reference to selectively decoupled and NOE enhancement ^{1}H NMR spectra; ^{13}C DEPT NMR ($CDCl_3$; 50.3 MHz) δ [ppm]: 23.73 (CH), 25.15 (CH), 26.43 (CH), 27.78 (CH),

34.14 (CH), 46.25 (CH), 47.90 (CH), 51.02 (CH_2), 51.83 (CH), 55.36 (CH_2); IR (nujol) $\nu_{max.}$[cm^{-1}]: 1412, 1375, 1343, 1328, 1303, 1293 (SO_2), 1246, 1236, 1159, 1147 (SO_2), 1097, 945, 914, 896, 851, 822, 773, 741, 711; MS [EI] m/e (%): 360 (0.3; $(^{81,81}M+2)^+$), 358 (0.7), 356 (0.3), 277 (100), 275 (98), 241 (7), 213 (6), 211 (11), 209 (7), 195 (16), 159 (75), 157 (77), 131 (70), 105 (14), 104 (15), 103 (18), 91 (58), 79 (99), 78 (98).

Evaporation of the recrystallisation filtrate gave an orange oil (79 mg) found by ^1H and ^{13}C NMR analyses to contain further dibromide (538) (est. 50 mg - total 89 mg, 75% yield) and at least three unidentified sulphone products (no starting diene (507) remaining). TLC (silica; ether) analysis indicated the presence of two bands, R_f 0.47 (coincidental with dibromide (538)) and R_f 0.34; these were separated by preparative TLC (silica; ether) and each found to be a mixture of sulphone products (at least one unsaturated compound in each mixture) of which only (538) [higher R_f band] was identified.

5. FVP of 4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide based systems

a. FVP of exo- and endo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (508), (329)

i. exo-4-Thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (508)

FVP [62°C, 750°C, 2 x 10^{-3} mm Hg] of the title compound (508) (9 mg, 4.5 x 10^{-2} mmol) gave a pyrolysate of crystalline solid and yellow oil. While this was still cold, deuteriochloroform was added, a little (0.5 mg) unidentified polymeric solid filtered off and the resultant solution analysed by ^1H NMR spectroscopy [chloroform

(3.6 mg) added for assessment of product yields] and GLC (5% carbowax; 50°C) [yields of hydrocarbons were also estimated by comparison with standard solutions of authentic materials]. The pyrolysate was found to contain starting sulphone (508) (est. 42% recovered), buta-1,3-diene (est. 5% yield), cyclohexa-1,3-diene (est. 11% yield on total starting sulphone (508)), benzene (16%), o-xylene (16%) and styrene (4%).

ii. endo-4-Thiatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 4,4-dioxide (329)

The pyrolysis conditions described by Aitken[33] were followed. FVP [65°C, 750°C, 4 x 10^{-3} mm Hg] of the title compound[33] (329) (13 mg, 6.6 x 10^{-2} mmol) gave a pyrolysate of colourless solid and yellow oil. Addition of deuteriochloroform to the cold pyrolysate followed by filtration to remove an unidentified polymeric solid (2 mg) gave a solution found by ^{1}H NMR and GLC (5% carbowax; 50°C) analyses to contain starting sulphone (329) (est. 28% recovered), cyclohexa-1,3-diene (est. 19% yield on total starting sulphone (329)), benzene (7%), o-xylene (10%), styrene (2%) and two unidentified volatile hydrocarbons (ca 5%). This product distribution is similar to that found by Aitken[33].

b. FVP of 8,9-disubstituted 4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene 4,4-dioxide systems

i. exo-4-Thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylic anhydride 4,4-dioxide (493a)

FVP [160-180°C, 600°C, 6 x 10^{-3} mm Hg] of the title compound (493a) (23.2 mg, 8.7 x 10^{-2} mmol) gave a colourless solid (7.6 mg), completely soluble in deuteriochloroform. Analysis by ^{1}H NMR spectroscopy (calibrated by addition of methylene chloride (19.2 mg)) indicated the presence of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-

dioxide (212) (est. 4.0 mg, 27% yield) - confirmed by TLC (silica; ether) - and maleic anhydride (est. 3.6 mg, 42% yield) only.

ii. Dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-exo-cis-8,9-dicarboxylate 4,4-dioxide (506)

α. FVP at 600°C

FVP [160°C, 600°C, 6 x 10^{-3} mm Hg] of the title compound (506) (38 mg, 0.12 mmol) gave a mixture of colourless solid and liquid. This was completely soluble in deuteriochloroform (0.6 ml): analysis by ^{1}H NMR spectroscopy (calibrated by addition of a measured quantity of methylene chloride) indicated the pyrolysate to comprise starting sulphone (506) (est. 23.0 mg, 61% recovered), cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (est. 7.2 mg, 35% yield on total starting sulphone (506)) and dimethyl maleate (est. 5.2 mg, 30% yield).

β. FVP at 700°C

FVP [160°C, 700°C, 6 x 10^{-3} mm Hg] of the title compound (506) (16 mg, 5.1 x 10^{-2} mmol) gave a pyrolysate consisting of a colourless solid and liquid. This was dissolved in deuteriochloroform - analysis by ^{1}H NMR spectroscopy indicated the absence of starting sulphone (506) [confirmed by TLC (silica; ether) analysis] and the presence of cis-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxide (212) (est. 2.7 mg, 31% yield), dimethyl maleate (est. 4.5 mg, 61%) and dimethyl fumarate (est. 2.3 mg, 31%). Yields were estimated from ^{1}H NMR by addition of a measured quantity of methylene chloride, and the presence of dimethyl maleate and fumarate products were confirmed by comparison of GLC retention times with authentic samples, and by GC-MS analysis.

c. FVP of 4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene 4,4-dioxide based systems

i. 4-Thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene 4,4-dioxide (507)

FVP [110°C, 600°C, 5 x 10^{-3} mm Hg] of the title compound (507) (15 mg, 7.7 x 10^{-2} mmol) gave a pyrolysate of a yellow liquid and a very small quantity of polymeric solid. The cold pyrolysate was treated with deuteriochloroform, filtered and the filtrate analysed by ^{1}H NMR spectroscopy (yields of products estimated from addition of a measured quantity of methylene chloride) and GLC (10% PEGA; 90°C) which indicated the presence of benzene (est. 5.4 mg, 90% yield) and styrene (est. 0.2 mg, 3%) only.

ii. Dimethyl exo-4-thiatricyclo[5.2.2.$0^{2,6}$]undeca-8,10-diene-8,9-dicarboxylate 4,4-dioxide (492a)

FVP [140°C, 650°C, 5 x 10^{-3} mm Hg] of the title compound (492a) (29.2 mg, 9.4 x 10^{-2} mmol) gave a pyrolysate of a light yellow liquid, found to be pure dimethyl phthalate (18.0 mg, 99% yield) on comparison of ^{1}H NMR and IR spectra with those of a commercial sample.

APPENDIX A: Crystal Structure Data for (208)

Crystal data for (208): $C_8H_{10}O_2S$, M = 170.23, monoclinic, space group $P2_1/c$ (No. 14), a = 9.286(2), b = 10.034(2), c = 9.187(2) Å, β = 107.16(2)°, U = 818(1) Å^3, Z = 4, D_c = 1.38 gcm^{-3}, F (000) = 360, μ (Mo-Kα) = 3.3 cm^{-1}. R = 0.037, R_w = 0.035 for 1636 reflections [293K, $2.0 \leq 2\theta \leq 56°$, $I \geq 3.0\sigma(I)$, Enraf-Nonius CAD-4 diffractometer, Mo-Kα X-radiation (graphite monochromator), λ = 0.71073 Å]. Unit weights gave a satisfactory analysis of variance and a goodness-of-fit of 0.49.

Selected bond lengths (Å) [e.s.d.'s in parenthesis]

S	O(1)	1.438(2)	C(3)	C(4)	1.501(5)
S	O(2)	1.441(2)	C(3)	C(6)	1.562(5)
S	C(1)	1.772(3)	C(4)	C(5)	1.309(7)
S	C(8)	1.775(3)	C(5)	C(6)	1.504(5)
C(1)	C(2)	1.515(4)	C(6)	C(7)	1.552(4)
C(2)	C(3)	1.558(4)	C(7)	C(8)	1.513(4)
C(2)	C(7)	1.567(4)			
C(1)	H(1A)	0.89(3)	C(5)	H(5)	1.00(5)
C(1)	H(1B)	0.92(3)	C(6)	H(6)	0.98(3)
C(2)	H(2)	0.96(3)	C(7)	H(7)	0.94(3)
C(3)	H(3)	0.92(3)	C(8)	H(8A)	0.93(4)
C(4)	H(4)	0.95(4)	C(8)	H(8B)	0.93(4)

Selected torsion angles (°)

C(8)	S	C(1)	C(2)	-33.4	C(2)	C(3)	C(6)	C(5)	113.4
C(1)	S	C(8)	C(7)	32.8	C(2)	C(3)	C(6)	C(7)	-0.2
S	C(1)	C(2)	C(3)	-76.3	C(4)	C(3)	C(6)	C(5)	-0.3
S	C(1)	C(2)	C(7)	24.1	C(4)	C(3)	C(6)	C(7)	-114.0

Selected torsion angles (°) [cont.]

C(1)	C(2)	C(3)	C(4)	-162.9	C(3)	C(4)	C(5)	C(6)	-0.4
C(1)	C(2)	C(3)	C(6)	112.8	C(4)	C(5)	C(6)	C(3)	0.4
C(7)	C(2)	C(3)	C(4)	84.6	C(4)	C(5)	C(6)	C(7)	88.6
C(7)	C(2)	C(3)	C(6)	0.2	C(3)	C(6)	C(7)	C(2)	0.2
C(1)	C(2)	C(7)	C(6)	-119.0	C(3)	C(6)	C(7)	C(8)	-112.4
C(1)	C(2)	C(7)	C(8)	-1.2	C(5)	C(6)	C(7)	C(2)	-84.9
C(3)	C(2)	C(7)	C(6)	-0.2	C(5)	C(6)	C(7)	C(8)	162.4
C(3)	C(2)	C(7)	C(8)	117.5	C(2)	C(7)	C(8)	S	-22.2
C(2)	C(3)	C(4)	C(5)	-87.4	C(6)	C(7)	C(8)	S	78.2
C(6)	C(3)	C(4)	C(5)	0.4					

Selected bond angles (°) [e.s.d.'s in parenthesis]

O(1)	S	O(2)	116.6(1)	C(2)	C(3)	C(6)	90.0(2)
O(1)	S	C(1)	111.7(2)	C(4)	C(3)	C(6)	84.8(3)
O(1)	S	C(8)	112.5(2)	C(3)	C(4)	C(5)	95.4(4)
O(2)	S	C(1)	110.0(2)	C(4)	C(5)	C(6)	94.3(4)
O(2)	S	C(8)	109.1(2)	C(3)	C(6)	C(5)	85.5(3)
C(1)	S	C(8)	94.8(2)	C(3)	C(6)	C(7)	90.1(2)
S	C(1)	C(2)	105.7(2)	C(5)	C(6)	C(7)	113.6(3)
C(1)	C(2)	C(3)	116.9(3)	C(2)	C(7)	C(6)	90.1(2)
C(1)	C(2)	C(7)	110.1(3)	C(2)	C(7)	C(8)	110.3(3)
C(3)	C(2)	C(7)	89.7(2)	C(6)	C(7)	C(8)	115.9(3)
C(2)	C(3)	C(4)	113.6(3)	S	C(8)	C(7)	105.9(2)
S	C(1)	H(1A)	108(2)	C(4)	C(5)	H(5)	135(3)
S	C(1)	H(1B)	106(2)	C(6)	C(5)	H(5)	130(3)
C(2)	C(1)	H(1A)	115(2)	C(3)	C(6)	H(6)	126(2)
C(2)	C(1)	H(1B)	112(2)	C(5)	C(6)	H(6)	120(2)
H(1A)	C(1)	H(1B)	109(3)	C(7)	C(6)	H(6)	115(2)

Selected bond angles (°) [e.s.d.'s in parenthesis] (Cont.)

C(1)	C(2)	H(2)	109(2)	C(2)	C(7)	H(7)	115(2)
C(3)	C(2)	H(2)	114(2)	C(6)	C(7)	H(7)	112(2)
C(7)	C(2)	H(2)	116(2)	C(8)	C(7)	H(7)	112(2)
C(2)	C(3)	H(3)	116(2)	S	C(8)	H(8A)	107(2)
C(4)	C(3)	H(3)	120(2)	S	C(8)	H(8B)	108(2)
C(6)	C(3)	H(3)	124(2)	C(7)	C(8)	H(8A)	110(2)
C(3)	C(4)	H(4)	127(3)	C(7)	C(8)	H(8B)	112(2)
C(5)	C(4)	H(4)	137(3)	H(8A)	C(8)	H(8B)	113(3)

Selected least-squares planes [e.s.d.'s in parenthesis]

Equations of the planes are of the form: $p*x + q*y + r*z - s = 0$ where x, y and z are the orthogonalised coordinates.

Plane no.	p	q	r	s	Atoms	Dist. (Å)
1	0.0672	0.5859	-0.8076	-5.6852	C(1)	-0.004(2)
					C(2)	0.007(2)
					C(7)	-0.007(2)
					C(8)	0.004(2)
2	-0.8170	0.1255	-0.5628	-4.5789	C(2)	-0.002(2)
					C(3)	0.002(2)
					C(6)	-0.002(2)
					C(7)	0.002(2)
3	0.1387	0.6114	-0.7791	-3.9930	C(3)	-0.002(2)
					C(4)	0.003(3)
					C(5)	-0.003(3)
					C(6)	0.002(2)
4	0.5949	0.5824	-0.5539	-4.3026	C(1)	0.000
					S	0.000
					C(8)	0.000

5	0.2716	-0.7863	-0.5550	-4.6158	S	0.000
					O(1)	0.000
					O(2)	0.000

Dihedral angles between planes

Plane no.	Plane no.	Dihedral angle
1	2	61.8
1	3	4.6
1	4	34.0
1	5	89.7
2	3	66.3
2	4	95.8
2	5	90.5
3	4	29.5
3	5	90.6
4	5	89.4

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Dehydrogenative Vacuum Pyrolysis: a Novel Synthetic Technique. Conversion of Cyclo-octa-1,5-diene into Styrene and Related Reactions

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Vacuum pyrolysis in the presence of palladium on charcoal of the 3,3-dioxide (**1**) of 3-thiabicyclo[3.2.0]-heptane-6,7-dicarboxylic anhydride gave, without undesirable disproportionation, phthalic anhydride, also obtained from *cis*-2,3-divinylsuccinic anhydride (**2**) and *cis*-1,2,3,6-tetrahydrophthalic anhydride (**5**), while cyclo-octa-1,5-diene (**7**) and the disulphone (**6**) each gave styrene.

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Chemical Communications 1983

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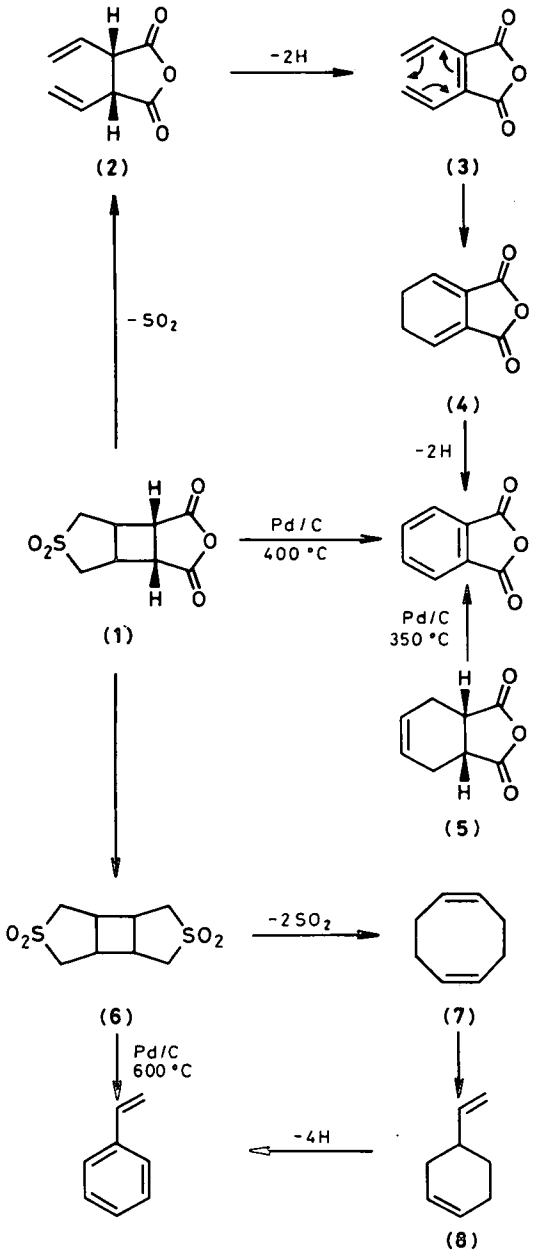
Over the past decade flash vacuum pyrolysis (F.V.P.) has played an increasingly important role in preparative organic chemistry.[1] We now report an extension of this technique of potentially wide application based on the simultaneous use of a dehydrogenation catalyst.

The origin of our procedure lies in our earlier observation[2] that F.V.P. of the 3,3-dioxide (**1**) of 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic anhydride, easily prepared by photolysis of equimolar amounts of butadiene sulphone and maleic anhydride, gave *cis*-2,3-divinylsuccinic anhydride (**2**) in 80% yield. We reasoned that removal of the ring-junction hydrogens from (**2**) should lead to electrocyclisation of the resulting (**3**) to (**4**) which would afford phthalic anhydride under dehydrogenating conditions (Scheme 1). This was readily accomplished *in a single step* with the same apparatus[3] by subliming (**1**) at 10^{-3} mmHg and 400 °C through a catalyst bed of 5% palladium on activated carbon.† In accord with this, similar pyrolyses of *cis*-2,3-divinylsuccinic anhydride (**2**) at 425 °C and of *cis*-1,2,3,6-tetrahydrophthalic anhydride (**5**) at 350 °C, also gave phthalic anhydride (48—52%). It is noteworthy that in none of these pyrolyses did significant and undesirable disproportionation to hydrogenated products take place. The method is therefore superior to the corresponding dehydrogenation in solution wherein, for example, *cis*-1,2,3,6-tetrahydrophthalic acid is converted into a 2:1 mixture of phthalic acid and cyclohexane-1,2-dicarboxylic acid, respectively, by palladium black in boiling tetrahydrofuran.[4]

We also pyrolysed the crystalline, high-melting (>320 °C) disulphone (**6**), prepared from (**1**) by successive esterification, reduction to the diol, conversion into the bistoluene-*p*-sulphonate, treatment with Na_2S, and essentially quantitative oxidation of the resulting sulphide with *m*-chloroperoxybenzoic acid in methylene chloride.‡ The sparingly volatile (**6**) at 650 °C gave a mixture of 4-vinylcyclohexene (**8**) and cyclo-octa-1,5-diene (**7**) in the ratio *ca.* 4:1 as determined by g.l.c. (10% Pega at 100 °C). Butadiene was also detected by n.m.r., but was not quantified. Since heating of cyclo-octa-1,5-diene in the gas phase causes a rearrangement to 4-vinylcyclohexene as well as giving minor amounts of butadiene,[5] it is reasonable to conclude that this compound is an intermediate in the thermal decomposition of (**6**), although its mode of formation is not certain.

When we subjected (**6**) to pyrolysis over 5% palladium on activated carbon catalyst at 600 °C, both rearrangement and dehydrogenation occurred simultaneously. As a result, styrene was obtained as the major product, albeit in low yield (12%), together with benzene (4%), toluene (2%), xylenes (2%), and ethylbenzene (2%). Much better yields of styrene at 45%



Scheme 1

† The catalyst, available from Alpha Division in 6—8 mesh pellets, is packed into the horizontal pyrolysis tube (35 × 2.3 cm, i.d.) between a coarse silica frit 12 cm from the exit end and a loose plug of quartz wool. Prior to each pyrolysis, it is conditioned by baking at 700 °C until a pressure of 10^{-3} mmHg is obtained.

‡ Satisfactory elemental analytical data were obtained for compound (**6**).

conversion were obtained by direct pyrolysis of cyclo-octa-1,5-diene (7) under dehydrogenating conditions. At 650 °C with 5% palladium on activated carbon catalyst, the crude pyrolysis product consisted of styrene (62%), xylenes (3%), toluene (9%), and benzene (26%). No ethylbenzene was detected.

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cis-Bromination of a Non-conjugated Cyclic Alkene. Unprecedented Electrophilic Stereoselection by Means of a Remote SO_2 Group

J. I. G. Cadogan,[a] Donald K. Cameron,[b] Ian Gosney,[b] Rona M. Highcock,[a] and Stephen F. Newlands[b]

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Contrary to expectation, addition of molecular bromine to 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (**1**) yields substantial amounts of the *cis*-1,2-dibromide (confirmed by *X*-ray diffraction), suggesting that the remote SO_2 group exerts an extraordinary directive influence by means of a long-range Coulomb interaction that stabilises an open carbocation intermediate at the expense of the usually favoured bridged bromonium ion.

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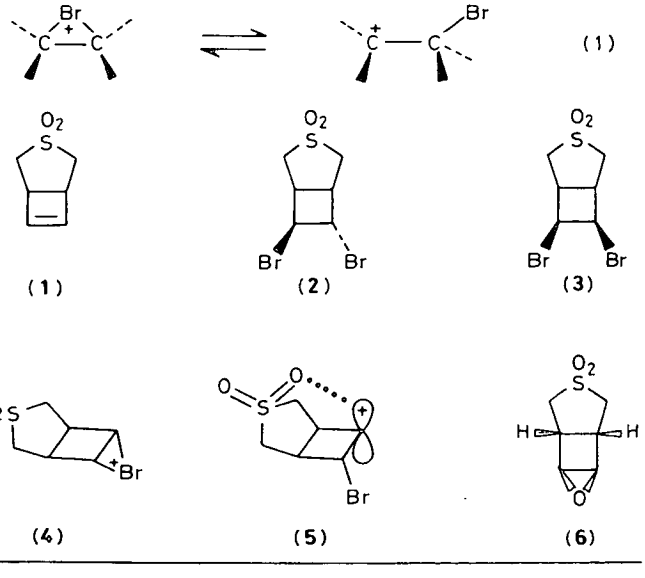
Formation of *cis*-1,2-dibromides by bromination of alkenes under ionic conditions is rare.[1] In the few cases reported, *syn*-addition is made kinetically attractive by the presence of conjugating groups on the double bond that stabilise open carbocations *vis-à-vis* a cyclic bromonium ion, equation (1). When such features are absent, the overwhelming preference is for *trans*-bromination. One notable exception is the reported[2] formation of a *cis*-1,2-dibromide (albeit as a 30:70 mixture with its *trans*-isomer) from Dewar benzene, but the compound was too unstable to be isolated and characterisation rested on chemical evidence. We now report another example, this time fully authenticated by a crystal structure determination, in which *syn*-addition to an isolated double bond is unexpectedly brought about by a favourable long-range Coulomb interaction between a remote SO_2 group and the open carbocation.

The compound in question is the bicyclic sulphone (**1**) formed by oxidative decarboxylation of the photoadduct of 2,5-dihydrothiophene 1,1-dioxide with maleic anhydride.[3] In contradistinction to the general behaviour of other non-conjugated alkenes, electrophilic addition of bromine to (**1**) in methylene chloride proceeded sluggishly and gave a 1:1 mixture (by n.m.r.) of isomeric dibromides which could be separated readily by 'flash' chromatography. That the mixture represented a kinetically controlled product distribution was established by the stability of the isomeric dibromides to the conditions of reaction. The structural assignment of one of the isomers, isolated as colourless rhombs (m.p. 160—163 °C), to the *trans*-dibromide (**2**)† followed convincingly from its ^{13}C n.m.r. spectrum which exhibited six signals at δ 54.17, 52.03, 49.32, 48.28, 42.28, and 39.45. The ^{13}C n.m.r. spectrum of the second isomer, also obtained in a pure state as stable colourless needles (m.p. 168–168.5 °C), was entirely compatible with the symmetry of the *cis*-dibromide structure (**3**) in that only three signals appeared, at $\delta(CDCl_3)$ 53.39, 48.54, and 43.30. Because bromine addition to non-conjugated alkenes normally takes place with *trans*-stereochemistry, the structure of (**3**), shown in Figure 1 with relevant bond parameters, was validated by an *X*-ray diffraction study.‡

Formation of the *cis*-dibromide (**3**) at the expense of an equal amount of the expected *trans*-product (**2**) requires the intermediacy of the open carbocation (**5**) and subsequent *syn*-attack by Br^- at a rate that is competitive with *anti*-collapse of the bromonium ion (**4**). From an inspection of Dreiding models, there is no question that the SO_2 group can provide sufficient steric bias to divert the incoming Br^- away from the *anti*-face and hence cause the *syn*-attachment of two



† All new compounds were characterised by combustion analysis as well as by ^1H and ^{13}C n.m.r., i.r., and mass spectrometry

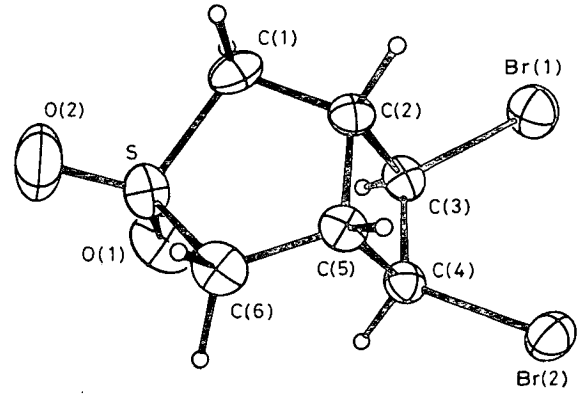


Figure 1. Molecular structure of (**3**). Selected bond lengths (Å) are: S–O(1) 1.436(5), S–O(2) 1.435(5), S–C(1) 1.791(8), S–C(6) 1.793(7), C(1)–C(2) 1.527(9), C(2)–C(3) 1.520(9), C(2)–C(5) 1.574(9), C(3)–C(4) 1.527(9), C(3)–Br(1) 1.947(6), C(4)–C(5) 1.544(9), C(4)–Br(2) 1.962(6), C(5)–C(6) 1.520(9).

‡ *Crystal data:* (**3**), $C_6H_8Br_2O_2S$, M = 304.01, monoclinic, space group $P2_1/c$ (No. 14), a = 10.430(3), b = 6.650(2), c = 12.723(8) Å, β = 91.20(4)°, U = 882(1) Å^3, Z = 4, D_c = 2.29 g cm^{-3}, $F(000)$ = 584, $\mu(Mo\text{-}K_\alpha)$ = 92.8 cm^{-1}, R = 0.042, R_w = 0.047 for 1366 reflections [293 K, $1.0 \leq 2\theta \leq 56°$, $I \geq 3.0\sigma(I)$, Enraf-Nonius CAD-4 diffractometer, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.71073 Å]. A weighting scheme of the form $w^{-1} = \sigma^2(F) + (0.22 \times F)^2 + 1.8$ {where $\sigma(F) = [F^2 + 2F \times \sigma(F)]^{-\frac{1}{2}} - F$} gave a satisfactory analysis of variance and a goodness-of-fit of 1.05.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

large bromine atoms.§ We have also discounted intramolecular participation by the SO_2 group as the source of the *cis*-stereoselection. The *X*-ray structure of the alkene (**1**) shows a least distance of 3.23 Å between the *exo*-oxygen atom of the SO_2 group and the double bond,¶ making any bonding to the reaction centre in (**4**) unlikely, particularly as the SO_2 group is a very poor nucleophile. Furthermore, even if bonding could occur, it should lead to overall *syn*-addition, whereas there is an equal preference for *anti*-addition. In our view, the relaxation in the usual demand for bridging by bromine in (**4**) is brought about by the unprecedented stabilising effect of a long-range Coulomb interaction between the highly polar SO_2 group and the carbocation centre as depicted in (**5**).

As a corollary to these findings we have observed the same type of proximity effect in the ring-opening of the *anti*-epoxide (**6**) with aqueous HBr (60%) in glacial acetic acid. This is borne out by the loss of the *trans*-stereospecificity usually associated with epoxides in which the effect of conjugation is absent.[5] Thus, on the basis of nuclear Overhauser enhancement studies, we found that the bromohydrins from (**6**) contained 37% of the *cis*-isomer, the formation of which demands the intermediacy of an open carbocation. In this connection it is of some significance that the reaction of the alkene (**1**) with *N*-bromoacetamide in aqueous acetone gives only a single bromohydrin which is derived by exclusive *anti*-attack on the bridged intermediate (**4**). This apparently paradoxical behaviour may be explained by hydration of the polar SO_2 group, resulting in a loss of its directive influence. This interpretation is supported by the observation that bromination of (**1**) in aqueous 1,2-dimethoxyethane proceeds normally to give, as the only product, the *trans*-1,2-dibromide (**2**).

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§ Even in the comparatively hindered system, 7,7-dimethylbicyclo-[3.2.0]hept-2-en-6-one, bromination occurs exclusively with *trans*-stereochemistry.[4]

¶ Full crystallographic data for (**1**) will be published elsewhere.

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The Sulphone Group as a Nucleophile: Intramolecular Formation of a Novel Thiadecanylium Tribromide *via* Addition of Bromine to a Double Bond in an Overcrowded Environment

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Instead of furnishing a normal bromide addition product, bromination of 4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (**1**) gives 5-bromo-1-oxo-10-oxa-1λ^{6}-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (**3**) through intramolecular reaction of the bromonium intermediate with the adjacent weakly nucleophilic sulphone group.

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Abnormal behaviour is rarely encountered in the electrophilic addition of bromine to an olefinic double bond despite this being one of the longest recognised and most widely studied reactions of alkenes.[1] We now report a unique reaction of an overcrowded alkene to which the addition of bromine is prematurely terminated by a remarkable transannular interaction between the bromonium intermediate and a sulphone group, hitherto not credited with being able to participate as a nucleophile.

Thus, reaction of novel 4-thiatricyclo[5.2.0.$0^{2,6}$]non-8-ene 4,4-dioxide (**1**) with bromine leads not to the normal dibromide, but to 5-bromo-1-oxo-10-oxa-1λ^6-thiatetracyclo[4.3.1.$0^{3,8}$.$0^{4,7}$]decan-1-ylium tribromide (**3**).

The synthesis of the tricyclic sulphone (**1**)† was achieved in five steps from the Diels–Alder adduct of cyclobutadiene with maleic anhydride. Its *syn*-cyclobutane structure was assigned on the basis of n.m.r. spectra‡ [including ^{1}H decoupling and nuclear Overhauser effect (n.O.e.) experiments] and by comparison with the *anti*-isomer (**4**) which can be obtained by conventional synthetic methods from the photo-adduct of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide[2] and maleic anhydride; the *anti*-orientation of the three rings in (**4**) was confirmed by *X*-ray analysis.§

When the olefin (**4**) was treated with an equimolar amount of bromine in methylene chloride at −78 °C reaction occurred in the normal way to give the *trans*-1,2-dibromide (**5**) (m.p. 135—136 °C, 89%) as evidenced by spectral data, especially its eight line ^{13}C n.m.r. spectrum [($CDCl_3$) δ 54.24, 53.76, 52.24, 51.80, 47.70, 44.48, 39.89, and 34.90]. In sharp contrast to this behaviour, the *syn*-isomer (**1**) consumed two equiv. of bromine at room temperature and gave an orange crystalline precipitate with the composition $C_8H_{10}Br_4O_2S$. Although reasonably stable, this compound decomposed on heating to 82—84 °C with loss of bromine. It was insoluble in diethyl ether, but dissolved in [$^2H_6$]acetone to give an orange solution which turned colourless almost immediately. Examination of this solution by ^{1}H n.m.r. spectroscopy revealed the presence of the starting olefin (**1**) and other products identified by g.l.c. analysis as being formed by irreversible bromination of the solvent. Structural evidence about the compound was obtained from n.m.r. spectroscopy in CD_3CN wherein reversal to free bromine and the olefin (**1**) resulted in an equilibrium mixture in which the compound predominated (60:40). The same equilibrium mixture was shown to be formed when the olefin (**1**) was treated with two equiv. of bromine in CD_3CN, while addition of excess bromine resulted in complete conversion into the olefin (**1**)–bromine complex. In keeping with the proposed structure (**3**) and its lack of symmetry, the ^{13}C n.m.r. spectrum of the complex displayed eight lines at δ (CD_3CN) 32.62, 34.77, 36.12, 42.88, 44.58, 45.12, 48.43, and 97.43.

The occurrence of a downfield resonance (δ 97.43) is consistent with the sulphonyl oxygen forming a bond to carbon. This is supported by the absence of i.r. bands characteristic of the SO_2 group and the observation of a corresponding resonance at δ 5.91 (1H, dd, *J* 6.0 and 4.3 Hz) in the 360 MHz ^{1}H n.m.r. spectrum of the compound which is in excellent agreement with the proposed structure (**3**).¶ A notable feature of the spectrum is the downfield position of *all resonances* relative to those of (**1**) as expected for such a positively charged species. The structure (**3**) is further supported by positive ion fast atom bombardment (f.a.b.) mass spectrometry which shows a strong peak (in thioglycerol) at *m/z* 249, 251 (1:1 doublet) for $[M-Br_3]^+$. Negative ion f.a.b. showed a strong Br^- signal, a small signal due to a Br_2^- cluster but no evidence for Br_3^-. Under electron impact conditions, (**3**) loses Br_2, yielding peaks no higher than *m/z* 170 which corresponds to the molecular ion of (**1**).

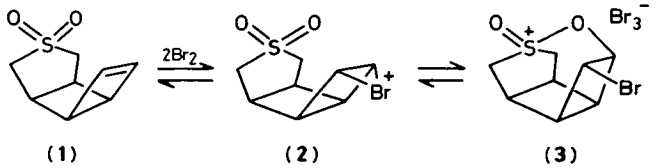
Nucleophilic behaviour by the sulphone group as reported above is without precedent.[3] It undoubtedly arises in this instance because the *syn*-sulphonyl oxygen, despite its extremely low nucleophilicity, is sited intramolecularly such that capture of the bromonium ion (**2**) from the *endo*-direction is stereoelectronically favourable. This is apparent from an inspection of Drieding models which shows a non-bonded distance of *ca.* 2.0 Å between the *syn*-oxygen atom of the sulphone group and the double bond in (**1**). In point of fact, it is this feature coupled with a molecular rigidity that inhibits the completion of the usual bromination pathway and leads to the stability of (**3**).

† All new compounds were characterised by combustion analysis as well as by ^{1}H and ^{13}C n.m.r., i.r., and mass spectrometry.

‡ (**1**): ^{1}H n.m.r. (360 MHz) ($CDCl_3$) δ 2.81—2.90 (sym. m, 2H), 3.07—3.15 (sym. m, 2H), 3.25—3.32 (sym. m, 2H), 3.47—3.50 (sym. m, 2H), 6.39 (dist. dd, *J* 1.7 and 1.4 Hz, 2H); ^{13}C n.m.r. ($CDCl_3$) δ 32.25, 44.14, 52.61, and 140.63. (**4**): ^{1}H n.m.r. (360 MHz) ($CDCl_3$) δ 2.83—2.87 (sym. m, 2H), 2.97—3.03 (sym. m, 2H), 3.22—3.23 (sym. m, 2H), 3.24—3.30 (sym. m, 2H), and 6.34 (dist. dd, *J* 1.4 and 1.2 Hz, 2H); ^{13}C n.m.r. ($CDCl_3$) δ 34.44, 47.85, 53.96, and 141.19.

§ *Crystal data* for (**4**): $C_8H_{10}O_2S$, *M* = 170.23, monoclinic, space group $P2_1/c$ (No. 14), *a* = 9.286(2), *b* = 10.034(2), *c* = 9.187(2) Å, β = 107.16(2)°, *U* = 818(1) Å^3, *Z* = 4, D_c = 1.38 g cm^{-3}, *F*(000) = 360, μ(Mo-K_α) = 3.3 cm^{-1}. *R* = 0.037, R_w = 0.035 for 1636 reflections [293 K, 2.0 ≤ 2θ ≤ 56°, *I* ≥ 3.0 σ (*I*), Enraf–Nonius CAD-4 diffractometer, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.71073 Å]. Unit weights gave a satisfactory analysis of variance and a goodness-of-fit of 0.49. The atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986. Full crystallographic details will be published elsewhere.

¶ (**3**): ^{1}H n.m.r. (CD_3CN) (360 MHz) δ 3.31 (d of t, *J* 7.6 and 4.3 Hz, 1H), 3.61 (d of d, *J* 6.0 and 3.0 Hz, 1H), 3.67 (d of d, *J* 15.5 and 8.74 Hz, 1H), 3.78—3.90 (m, 4H), 4.17 (d of d of d, *J* 16.2, 8.7 and 1.1 Hz, 1H), 4.43 (d of d, *J* 16.2 and 1.9 Hz, 1H), 5.91 (d of d, *J* 6.0 and 4.3 Hz, 1H).



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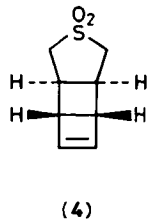
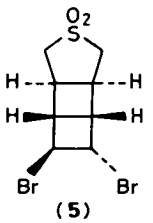
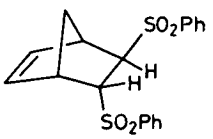


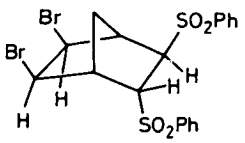
(4)



(5)



(6)



(7)

The capacity of the sulphone group to participate as an intramolecular nucleophile is further highlighted by the bromination of the norbornenyl derivative (**6**) to give *specifically exo,cis*-dibromide (**7**). This mode of addition is striking when compared with the exclusive *trans*-bromination of the corresponding dichloro-analogue under the same conditions.[4] It must similarly be attributed to the capture of the intermediate bromonium ion by the sulphone group, although in this particular case, there are no molecular constraints to restrict subsequent nucleophilic attack of Br^-, albeit from the normally hindered *exo*-direction.

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