Pyrolysis of tricyclic cyclobutane-fused sulfolanes as a route to *cis*-1,2-divinyl compounds and their Cope-derived products

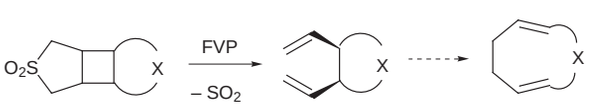
R. Alan Aitken,[a]† J. I. G. Cadogan,[b] Ian Gosney,[a] Caroline M. Humphries (née Buchan),[a] Leo M. McLaughlin[a] and Stuart J. Wyse[a]

[a] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b] *B. P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, UK TW16 7LN*

Received (in Cambridge) 30th November 1998, Accepted 8th January 1999

Functionalisation of the double bond of 3-thiabicyclo[3.2.0]hept-6-ene **3**, readily formed by hydrolysis of the [2+2] cycloadduct **1** of 3-sulfolene and maleic anhydride followed by oxidative bis-decarboxylation, gives tricyclic sulfones **5**–**7** and **9** with the bicyclo[3.3.0.0^{2,4}] skeleton. FVP of **3** results in stereospecific extrusion of SO_2 to give *Z*-hexa-1,3,5-triene which undergoes electrocylisation to give cyclohexa-1,3-diene while reaction of **3** with $LiAlH_4$ results in non-stereospecific extrusion to give *Z*- and *E*-hexa-1,3,5-triene. Upon FVP the tricyclic sulfones **5**–**7** and **9** lose SO_2 to give 7-membered ring products **16**–**19** by Cope rearrangement of the initially formed *cis*-1,2-divinyl intermediates **15**. The 1,3-dipolar cycloaddition of nitrile oxides and a nitrone to the double bond of **3** gives tricyclic sulfones with the tricyclo[5.3.0.0^{2,6}] skeleton and a wider variety of these can be prepared by conventional reactions of **1**. Upon FVP these lose SO_2 to give stable *cis*-1,2-divinyl compounds **23**, **24**, **37**–**40** and **41**–**44**. The Diels–Alder adducts **48** and **49** have been prepared from **3** and these behave differently upon FVP, losing SO_2 and butadiene to give tetrasubstituted benzenes, in the latter case by way of an unexpected tetracyclic intermediate.

Thermal extrusion of SO_2 from cyclic compounds has been widely used as a synthetic method and often allows access to products which would be difficult to obtain by other methods.[1] The pyrolysis of functionalised sulfolenes and sulfolanes is of particular importance and has found numerous applications.[2] Although there have been a few studies on cyclopropane-fused sulfolanes and their heterocyclic analogues, there were no examples of the corresponding method being applied to cyclobutane-fused sulfolanes prior to our work in the area. The general approach, summarised in Scheme 1, may be used to

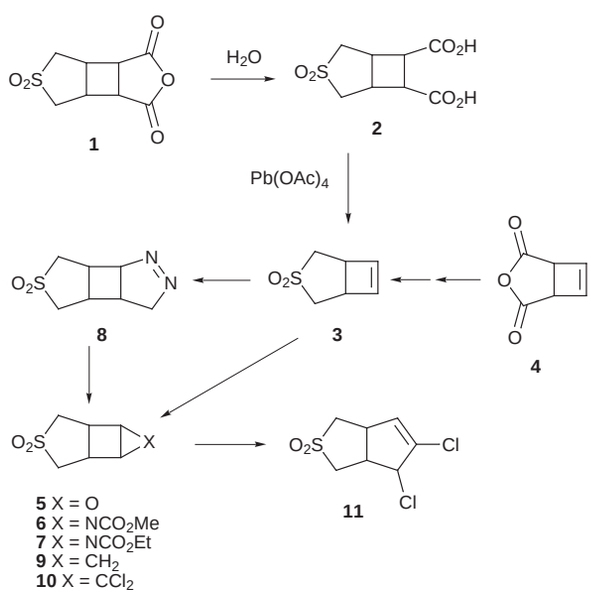


Scheme 1

access a wide range of *cis*-1,2-divinyl compounds and, depending upon the ring size involved, the products derived from their Cope rearrangement. We now present full details of the synthesis of cyclobutane-fused sulfolanes with an additional 3-, 5- or 6-membered fused ring and their reactivity under flash vacuum pyrolysis (FVP) conditions.[3]

Results and discussion

A convenient starting point for the synthesis is the tricyclic anhydride **1** whose preparation by photochemical [2 + 2] cycloaddition of 3-sulfolene (2,5-dihydrothiophene 1,1-dioxide) with maleic anhydride in acetone was reported by Shaikhrazieva and co-workers in 1972.[4] Using this method, the anhydride **1**, which formed the basis of all the subsequent synthetic work, was routinely prepared on a 50–100 g scale. For preparation of systems with fused 5-, 4- and 3-membered rings we envisaged the bicyclic alkene **3** as being a key intermediate and this was obtained by hydrolysis of **1** to the corresponding diacid **2** followed by oxidative bis-decarboxylation using lead tetraacetate in pyridine[5] (Scheme 2). The latter reaction was found

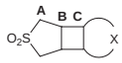


Scheme 2

to be rather problematic but by using precisely the conditions given in the experimental section, the target alkene **3** was obtained reproducibly in pure form, albeit in a rather low yield of 24%. Because of the low yield we also examined an alternative route to **3** from the bicyclic anhydride **4** whose utility as an acetylene equivalent has already been described.[6] It was found that **4** could indeed be converted into **3** by a sequence of conventional steps involving $LiAlH_4$ reduction to give the

† Present address: School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, UK KY16 9ST. E-mail raa@st-and.ac.uk

Table 1 ^{13}C NMR data for the bi- and tri-cyclic sulfones (δ_C)

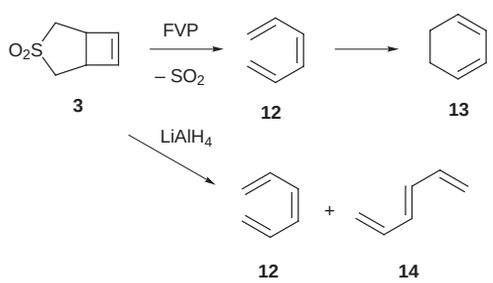


Compound	**A** signals	**B** signals	**C** signals	Other signals
3	52.0	41.0	139.0	—
5	49.7	40.8	56.5	—
8	54.1, 53.2	38.1, 37.9	90.0, 32.7	84.0
20	52.5, 52.3	37.4 (2 C)	82.1, 41.5	158.4, 130.4, 129.1, 127.7, 127.0
21	53.5, 53.1	37.3 (2 C)	81.9, 41.5	161.3, 157.6, 128.4, 119.8, 114.4, 55.3
26	53.0	35.0	42.3	177.8, 24.9
27	53.0	35.2	42.6	176.9, 132.6, 128.8, 128.4, 127.3
28	53.2	33.3	43.0	171.9, 51.9
30	54.7	33.3	41.6	60.5
31	53.7	36.8	37.8	69.1, 33.0
32	54.1	33.4	38.0	145.3, 132.2, 130.0, 127.7, 68.7, 21.5
33	54.6	36.2	43.0	73.2
34	54.6	36.0	46.0	38.3
36	55.0	36.7	41.8	139.1, 128.3, 128.0, 125.8, 59.1 (3 C)

corresponding diol, conversion into the ditosylate, reaction with sodium sulfide and finally *S*-oxidation. However the overall yield for this sequence was only 50% and the preparation of the starting material **4** involves the rather hazardous photolyis of a solution containing a high proportion of liquid acetylene;[7] consequently the more straightforward two-step route from **1** was generally used.

Some time ago we reported that the double bond in a variety of unsaturated sulfones including **3** was surprisingly unreactive towards addition of electrophilic species such as nitrenes.[8] This was reflected in high ionisation energies as determined by photoelectron spectroscopy and was attributed to deactivation by the sulfone group through a combination of through-bond and through-space orbital interactions. This feature limited the range of bicyclo[3.3.0.0^{2,4}] products which could be obtained and the alkene **3** failed to react with phenyldiazomethane, diphenyldiazomethane or phenyl azide under thermal or photochemical conditions, with ethyl diazoacetate under photochemical or rhodium catalysed conditions, with phthalimidonitrene and with difluorocarbene. The compound was however successfully oxidised using performic acid to give the epoxide **5** (39%). Although thermal reaction of **3** with ethyl azidoformate and reaction with ethoxycarbonylnitrene from α-elimination both failed, the aziridines **6** and **7** were obtained in around 30% yield by photolysis of **3** in the neat alkyl azidoformates and **7** could also be obtained by reaction with ethoxycarbonylnitrene from α-elimination under phase-transfer conditions.[9] The cyclopropane **9** was prepared in 40% overall yield by reaction of **3** with diazomethane to give **8** followed by photolysis in acetonitrile. An attempt to form the dichlorocarbene adduct **10** led rather unexpectedly to the formation of the isomer **11** resulting from rearrangement with 1,2-migration of a chlorine atom, a process well known for strained bi- and tri-cyclic dichlorocyclopropanes.[10] Thus reaction of the alkene **3** with bromodichloromethyl(phenyl)mercury[11] in boiling benzene gave only **11**, while reaction with dichlorocarbene from α-elimination under phase-transfer conditions[12] gave a crude product shown spectroscopically to contain a 1 : 1 mixture of **10** and **11** but this was largely converted into **11** upon purification. The tricyclic compounds obtained gave the expected analytical and spectroscopic data with the ^{13}C NMR signals for the carbon atoms adjacent to SO_2 coming consistently in the range δ_C 52–55 and those for the remaining carbons of the sulfolane ring in the range δ_C 33–41 (Table 1).

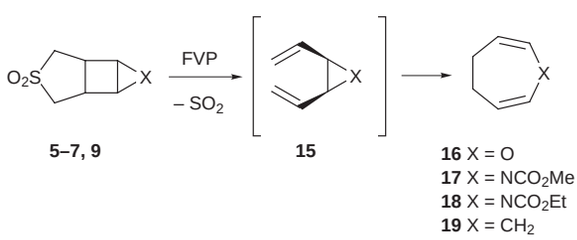
With a range of tricyclic sulfones in hand we were in a position to examine their pyrolytic behaviour. When the alkene **3** was subjected to FVP at 500 °C and 10^{-3}–10^{-2} Torr the only non-gaseous product was cyclohexa-1,3-diene **13** isolated in almost quantitative yield. We believe that this is formed by electrocyclisation of *Z*-hexa-1,3,5-triene **12** formed by the expected



Scheme 3

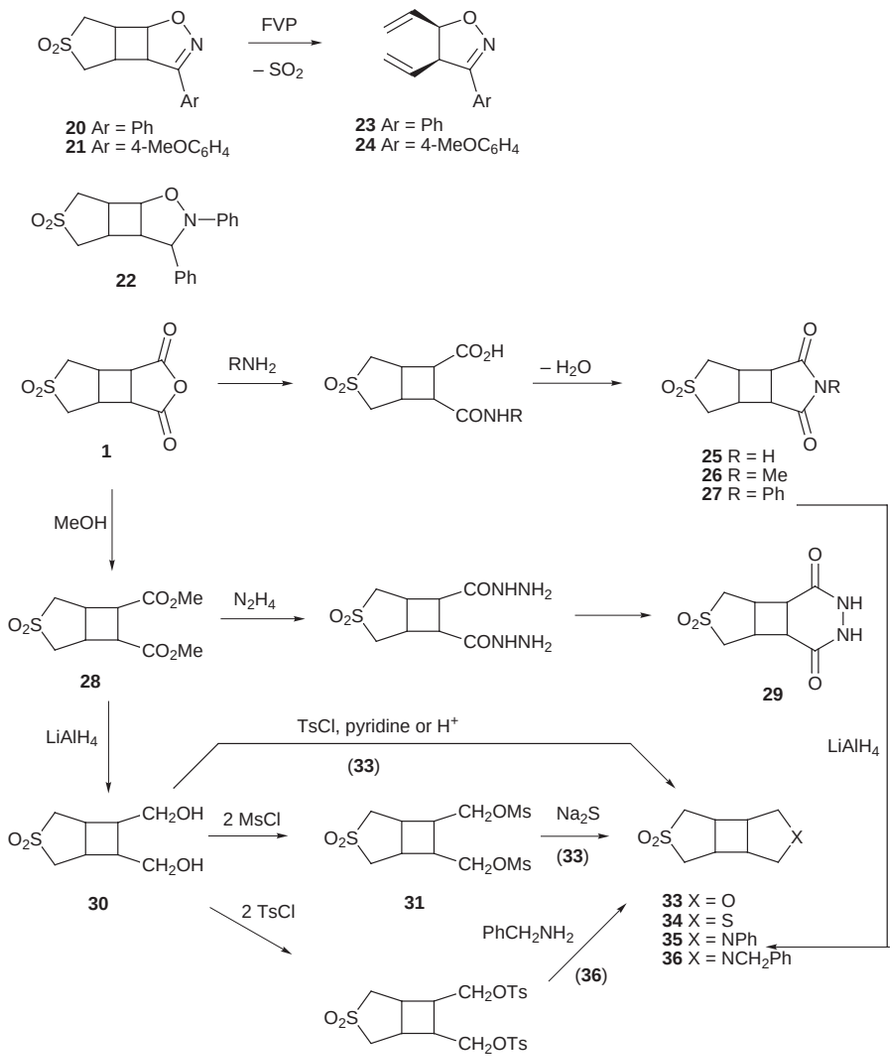
extrusion of SO_2 (Scheme 3). Evidence in support of this was obtained by FVP at the lower temperature of 400 °C. Under these conditions the alkene **3** was partly unreacted but the hydrocarbon products now consisted of **12** and **13** in a 1 : 3 ratio with the identity of **12** being confirmed by comparison of its ^1H NMR spectrum with the reported data.[13] It was of interest to compare the behaviour of the alkene **3** under the reductive extrusion conditions with $LiAlH_4$ successfully used by Gaoni in similar systems.[14] This produced a 1 : 1 mixture of *Z*- and *E*-hexa-1,3,5-trienes **12** and **14** identified by comparison with an authentic sample.[15] Interconversion of the two isomers was shown not to occur under these conditions so we conclude that, while the thermal extrusion stereospecifically gives the *Z* alkene **12**, the reductive solution extrusion method is completely non-stereospecific.

The behaviour of **5**–**9** upon FVP was now examined. The epoxide **5** underwent complete reaction at 580 °C to give 55% yield of a product which was identified by comparison of its ^1H and ^{13}C NMR data with the literature values[16] as 4,5-dihydrooxepine **16**. As shown in Scheme 4, this most likely



Scheme 4

results from initial extrusion of SO_2 to give *cis*-2,3-divinyloxirane **15** which undergoes Cope rearrangement to give **16**. Similar results were obtained for the aziridines **6** and **7** which gave the corresponding 4,5-dihydroazepines **17** and **18** isolated in 10–14% yield after preparative TLC. The cyclopropane **9**



Scheme 5

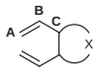
underwent complete reaction at 475 °C to give an 80% yield of cyclohepta-1,4-diene **19** identified by comparison with an authentic sample.[17] A somewhat more complex result was obtained by FVP of the diazomethane adduct **8** at 475 °C. The major product was still **19** (27%) but this was now accompanied by seven other isomers of C_7H_{10} (39%) and two of C_7H_8 (6%). The extrusion of both N_2 and SO_2 obviously allows a variety of additional reactions of the intermediate diradicals leading to isomeric products.

Following the successful addition of diazomethane to **3** to give **8** we envisaged formation of a range of sulfones with the tricyclo[5.3.0.0^{2,6}] skeleton by 1,3-dipolar cycloaddition to the alkene **3**. Reaction with benzonitrile oxide, *p*-anisonitrile oxide and *C*,*N*-diphenylnitrone did afford the expected adducts **20**, **21** and **22** in 19–45% yield but the alkene proved to be a rather poor dipolarophile and failed to react with nitrile imines, nitrile sulfides and an azomethine imine.

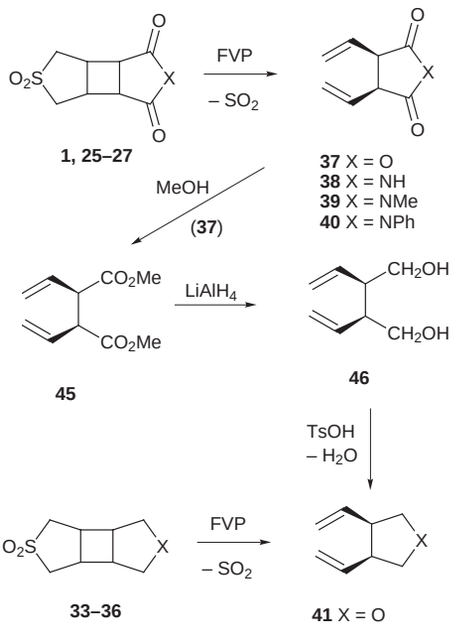
Because of the limited applicability of this approach we decided to prepare a wider range of tricyclo[5.3.0.0^{2,6}] systems by conventional transformations of the anhydride **1** (Scheme 5). Following the method of Shaikhrazieva and co-workers,[4] the anhydride **1** was reacted with aniline to give the acid amide which upon dehydration afforded the *N*-phenylimide **27**. Using the same method with ammonia or methylamine similarly gave the imides **25** and **26** and the former could also be prepared directly by photochemical [2 + 2] cycloaddition of 3-sulfolene and maleimide. Methanolysis of **1** gave the diester **28** which upon reaction with hydrazine followed by sublimation gave the cyclic hydrazide **29**. Access to the reduced compounds **33**–**36** was gained using the diol **30**, readily formed by reduction of the diester **28** with $LiAlH_4$. Dehydrative cyclisation of the diol **30** directly afforded **33** while conversion into the dimesylate **31** and reaction with sodium sulfide gave **34** and conversion into the ditosylate **32** and reaction with benzylamine gave **36**. The *N*-phenyl compound **35** was prepared by reduction of **27** using $LiAlH_4$. These tricyclic derivatives again showed a highly consistent pattern of ^{13}C NMR signals (Table 1).

When these compounds were subjected to FVP they again underwent clean extrusion of SO_2 but the divinyl compounds were now isolated as stable products. Thus, **20** and **21** gave the *cis*-4,5-divinylisoxazoles **23** (19%) and **24** (33%) respectively, at 500 °C. The anhydride **1** and its imide analogues **25**–**27** required temperatures of 625–630 °C for complete reaction but the yields of **37**–**40** (52–80%) were much better (Scheme 6). The reduced systems **33**, **34** and **36** similarly gave the *cis*-divinyl products **41**, **42** and **44** in moderate yields of 25–62% but the *N*-phenyl compound **35** did not react satisfactorily. All the divinyl compounds gave the expected analytical and spectroscopic data and again a consistent pattern was evident in their ^{13}C NMR data (Table 2). Correlation between the two series of compounds was achieved by methanolysis of **37** from FVP of **1** to give the diester **45**, reduction to the diol **46** and dehydrative cyclisation to give **41**, identical to the product from FVP of **33**. The pyrolysis of the cyclic hydrazide **29** also afforded a stable divinyl compound **47** (68%) and in this case the product was unusual in showing eight ^{13}C NMR signals despite its apparent symmetry. We attribute this to its existence in a conformation in which one vinyl group

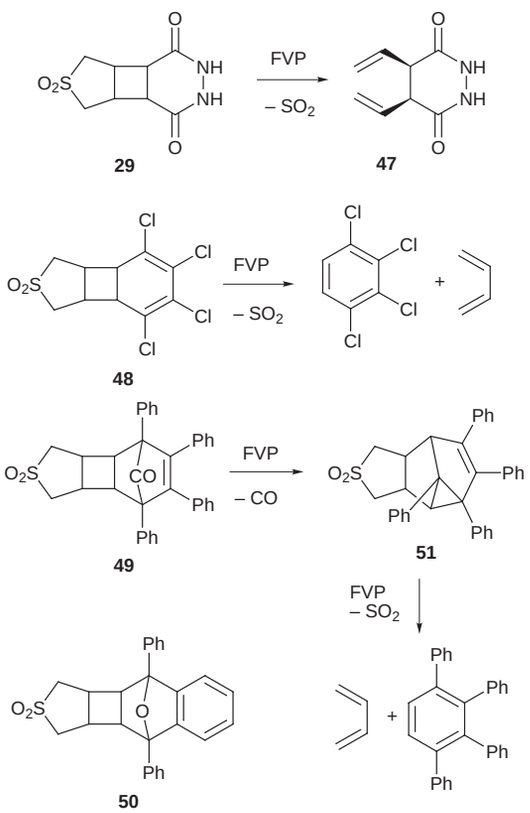
Table 2 ^{13}C NMR data for the divinyl compounds (δ_C)



Compound	**A** signals	**B** signals	**C** signals	Other signals
24	121.5, 120.2	132.0, 131.8	86.1, 55.2	160.9, 158.5, 128.5, 119.9, 113.9, 55.3
37	122.1	127.3	48.9	170.4
39	121.2	129.6	49.8	176.6, 25.0
40	121.3	126.2	48.9	175.4, 131.7, 129.6, 128.9, 128.4
41	116.1	135.8	47.5	71.9
42	116.3	136.3	51.1	34.8
45	119.0	132.6	51.5	171.4, 52.5
46	117.7	137.5	47.8	63.5
47	120.8, 119.6	132.9, 131.6	48.2, 47.1	174.8, 174.3
53	122.1, 118.0	135.9, 126.7	52.4, 47.7	170.8, 170.2, 21.1
55	123.0, 117.6	133.8, 126.5	56.1, 52.9	172.5, 169.6, 20.0



Scheme 6



Scheme 7

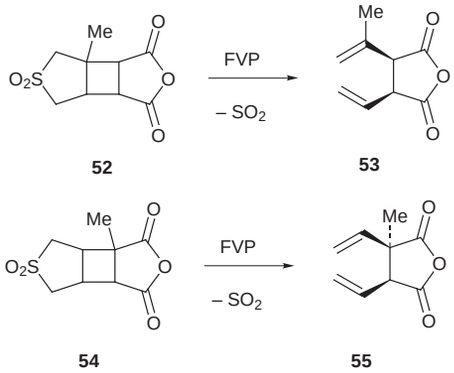
is axial and the other equatorial, thus making the groups non-equivalent on the NMR time-scale.

Some further more complex cyclobutane-fused sulfolanes were obtained by Diels–Alder cycloaddition of the alkene **3**. Reaction of **3** with tetrachlorothiophene 1,1-dioxide, which has been shown to undergo cycloaddition to a wide range of dienophiles with concomitant extrusion of SO_2,[18] took the expected course to give the adduct **48**. The corresponding reactions with tetraphenylcyclopentadienone and 1,3-diphenylisobenzofuran gave the adducts **49** and **50** respectively (Scheme 7). The pyrolysis of both **48** and **49** took an unexpected course and in each case the final products were SO_2, butadiene and a benzene derivative. For **48** the thermal [2 + 2] cycloreversion to give 1,2,3,4-tetrachlorobenzene is obviously favoured over the normal extrusion of SO_2 to form the 1,2-divinyl compound and it is worth noting that, in the overall transformation of **3** and tetrachlorothiophene dioxide *via* **48** into tetrachlorobenzene, **3** acts as an acetylene equivalent. It might be assumed at first sight that **49** would react in exactly the same way as **48**, by extrusion of CO to give the cyclohexadiene analogous to **48** and then [2 + 2] cycloreversion. However FVP of **49** at 330 °C gave a 65% yield of a product fully characterised as the tetracyclic compound **51**. Its structure was clear from its ^{13}C NMR spectrum which contained only two alkene signals and signals at δ_C 62.5 (CH), 59.6 (4ry), 57.6 (4ry) and 53.9 (CH) corresponding to the saturated carbons of the tricyclic part of the structure. When this was subjected to FVP at 675 °C, 1,2,3,4-tetraphenylbenzene was formed together with butadiene. The driving force for the last process is clearly the same as in the reaction of **48** and we assume that the tetracyclic structure **51** is favoured over its simpler tricyclic isomer by relief of unfavourable steric interactions which would be present in the hexasubstituted benzene ring of the other isomer.

Finally, the fact that this chemistry is amenable to the specific introduction of substituents was demonstrated by preparation and pyrolysis of the methylated analogues of **1**, compounds **52** and **54**. These were prepared, respectively, by photochemical [2 + 2] cycloaddition between 3-methyl-3-sulfolene (isoprene sulfone) and maleic anhydride and between 3-sulfolene and citraconic anhydride. When they were subjected to FVP at 580 °C, the expected divinyl anhydrides **53** (69%) and **55** (86%) were produced (Scheme 8).

Experimental

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. Infrared spectra were recorded for



Scheme 8

solids as Nujol mulls and for liquids as thin films unless otherwise indicated, on a Perkin Elmer 157G instrument. NMR spectra were obtained for ^{1}H at 100 MHz on a Varian HA100 instrument or at 360 MHz on a Bruker WH360 instrument and for ^{13}C at 20 MHz on a Varian CFT20 or at 90 MHz on a Bruker WH360 instrument. All spectra were run on solutions in $CDCl_3$ unless otherwise indicated, with internal Me_4Si as internal reference. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants *J* are in Hz. Mass spectra were obtained on an AEI MS902 spectrometer using electron impact at 70 eV. GC was carried out using a Pye 104 instrument with a 2 m × 4.5 mm column of 10% PEGA on Chromosorb W and nitrogen as carrier gas.

The anhydride **1** was prepared by the literature method[4] involving photochemical reaction of 2,5-dihydrothiophene 1,1-dioxide and maleic anhydride in acetone [60%, mp 292–293 °C (lit.,[4] 292–293 °C)] and converted into the diacid **2** by dissolution in boiling water followed by evaporation to dryness [83%, mp 188–190 °C (lit.,[4] 194–195 °C)].

Preparation of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide 3

A solution of the diacid **2** (5.0 g, 21.4 mmol) in dry pyridine (50 cm^3) was saturated with oxygen by passing the gas through it for 15 min. Vacuum dried lead tetraacetate (14.2 g, 32 mmol) was then added in one portion and the mixture heated to 70 °C. After 20 min evolution of CO_2 was complete and the clear dark brown solution was added to 5% nitric acid (1 dm^3). The mixture was extracted with CH_2Cl_2 (3 × 250 cm^3) which was dried and evaporated and the residue was Kugelrohr distilled at 150–200 °C/0.1 Torr. Recrystallisation of the product from diisopropyl ether gave the *title compound* **3** (0.75 g, 24%) as long colourless flakes, mp 72–74 °C (Found: C, 50.1; H. 5.35. $C_6H_8O_2S$ requires C, 50.0; H, 5.5%); ν_{max}/cm^{-1} 1410, 1287, 1229, 1167, 1110, 942, 852 and 728; δ_H 6.18 (2 H, s, 6,7-H), 3.7–3.6 (2 H, m, 1,5-H) and 3.2–2.9 (4 H, m, 2,4-H); δ_C see Table 1; *m*/*z* 144 (M$^+$, 3%), 81 (5), 80 (M$^+$ − SO_2, 55), 79 (100) and 77 (30).

Epoxidation, aziridination and cyclopropanation of 3

3-Oxa-7-thiatricyclo[3.3.0.0^{2,4}]octane 7,7-dioxide 5. The alkene **3** (0.60 g, 4.2 mmol was added to a mixture of 30% hydrogen peroxide (10 cm^3) and 90% formic acid (40 cm^3) at room temperature over 20 min. The resulting solution was stirred at 50 °C for 48 h, at room temperature for 48 h and then evaporated to dryness. Trituration of the residual oil with ethanol gave the *title epoxide* **5** (0.26 g, 39%) as colourless crystals, mp 118–119 °C (Found: C, 45.15; H, 5.0. $C_6H_8O_3S$ requires C, 45.0; H, 5.0%); ν_{max}/cm^{-1} 1325, 1290, 1240, 1130, 855, 835 and 715; δ_H 3.95 (2 H, d, *J* 1.5, 2,4-H), 3.3–3.1 (4 H, m, 6,8-H) and 3.05–2.9 (2 H, m, 1,5-H); δ_C see Table 1; *m*/*z* 160 (M$^+$, 0.1%), 131 (0.3), 104 (3), 95 (44) and 94 (100).

7-Methoxycarbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide 6. A mixture of the alkene **3** (0.50 g, 3.5 mmol) and methyl azidoformate (1.50 g, 15 mmol) was irradiated with a 400 W medium-pressure mercury lamp for 18 h. Chromatography of the resulting brown oil (alumina, diethyl ether) gave a colourless solid which was recrystallised from diisopropyl ether–methanol (5:1) to afford the *title aziridine* **6** (0.22 g, 30%) as colourless crystals, mp 175–177 °C (Found: C, 44.2; H, 5.1; N, 6.2. $C_8H_{11}NO_4S$ requires C, 44.2; H, 5.1; N, 6.4%); ν_{max}/cm^{-1} 1716, 1305, 1280, 1140, 1102, 949, 928, 890, 862, 811, 806, 775 and 720; δ_H 3.81 (3 H, s, OMe), 3.3–3.2 (6 H, m, 1,2,4,5-H) and 2.98–2.88 (2 H, m, 6,8-H); *m*/*z* 217 (M$^+$, 0.1%), 186 (14), 152 (3), 151 (8), 139 (32), 138 (100), 95 (10), 94 (89), 67 (93) and 59 (50).

7-Ethoxycarbonyl-3-thia-7-azatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide 7. Reaction of the alkene **3** (0.50 g, 3.5 mmol) as above but using ethyl azidoformate (1.25 g, 10.9 mmol) gave a solid after chromatography which was recrystallised from diethyl ether–CH_2Cl_2 (4:1) to afford the *title aziridine* **7** (0.25 g, 31%) as colourless crystals, mp 142–143 °C (Found: C, 46.8; H, 5.7; N, 6.1. $C_9H_{13}NO_4S$ requires C, 46.7; H, 5.7; N, 6.1%); ν_{max}/cm^{-1} 1708, 1309, 1273, 1140, 1099, 1039, 900, 865, 812, 768 and 721; δ_H 4.25 (2 H, q, *J* 7, OCH_2), 3.26–3.20 (6 H, m, 1,2,4,5-H), 3.00–2.88 (2 H, m, 6,8-H) and 1.31 (3 H, t, *J* 7, CH_3); *m*/*z* 231 (M$^+$, 0.3%), 186 (12), 159 (5), 108 (23), 94 (32) and 80 (100).

The aziridine **7** could alternatively be prepared using the phase-transfer method of Seno and co-workers.[9] A solution of alkene **3** (72 mg, 0.5 mmol), ethyl 4-nitrophenylsulfonyloxycarbamate (145 mg, 0.5 mmol) and benzyltriethylammonium chloride (12 mg, 0.05 mmol) in CH_2Cl_2 (10 cm^3) was stirred vigorously with 1 M aqueous sodium bicarbonate (2 cm^3) for 4 h. Water (25 cm^3) was then added and the organic layer separated, washed with water, dried and evaporated. Chromatographic purification of the residue gave **7** (50 mg, 43%) with properties identical to those above.

4-Thia-8,9-diazatricyclo[5.3.0.0^{2,6}]dec-8-ene 4,4-dioxide 8. To a solution of the alkene **3** (0.50 g, 3.5 mmol) in diethyl ether (20 cm^3) was added diazomethane (20 mmol) in diethyl ether and the solution was kept at room temperature for 120 h. Partial evaporation followed by cooling at 0 °C led to crystallisation of the product which was filtered off to give the *title compound* **8** (0.50 g, 82%) as pale yellow needles, mp 157–158 °C (Found: C, 45.3; H, 5.4; N, 14.9. $C_7H_{10}N_2O_2S$ requires C, 45.1; H, 5.4; N, 15.0%); ν_{max}/cm^{-1} 1535, 1295, 1137, 888 and 686; δ_H 5.28 (1 H, m, 7-H), 4.60 (2 H, dd, *J* 2.5, 1, 10-H), 3.5–3.0 (5 H, m, 3,5,6-H) and 2.8–2.5 (2 H, m, 1,2-H); δ_C see Table 1; *m*/*z* 187 (M + H$^+$, 0.8%), 186 (M$^+$, 0.04), 93 (17), 91 (21), 79 (100) and 77 (50).

3-Thiatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide 9. A solution of the diazomethane adduct **8** (196 mg, 1.05 mmol) in dry acetonitrile (5 cm^3) was irradiated with a medium-pressure mercury lamp for 60 h. Evaporation and separation of the residue using preparative TLC (alumina, diethyl ether) followed by recrystallisation from hexane–diethyl ether (3:1) gave the *title cyclopropane* **9** (80 mg, 48%) as colourless needles, mp 94–95 °C (Found: C, 52.9; H, 6.4. $C_7H_{10}O_2S$ requires C, 53.1; H, 6.4%); ν_{max}/cm^{-1} 1302, 1290, 1250, 1197, 1169, 1122, 1094, 955, 920, 893 and 713; δ_H 3.24–3.12 (4 H, m, 2,4-H), 2.60 (2 H, m, 1,5-H), 1.71 (2 H, d, *J* 5.5, 6,8-H) and 0.96–0.76 (2 H, m, 7-H); *m*/*z* 158 (M$^+$, 0.6%), 94 (M$^+$ − SO_2, 18), 93 (63), 92 (36), 91 (37), 80 (13), 79 (100), 78 (25) and 77 (67).

7,8-Dichloro-3-thiabicyclo[3.3.0]oct-6-ene 3,3-dioxide 11. A solution of the alkene **3** (0.10 g, 0.69 mmol) and bromodichloromethyl(phenyl)mercury[11] in dry benzene (10 cm^3) was heated under reflux for 55 h. The solution was evaporated and the residual solid leached with hot chloroform (5 × 10 cm^3). Hydrogen sulfide gas was passed through the combined solution for 2 min and the solution was then filtered. Evaporation of the filtrate followed by preparative TLC (silica, CH_2Cl_2) gave

unreacted **3** (70 mg) and the *title compound* (6.2 mg, 4%) (13% on reacted **3**) as colourless needles, mp 143–144 °C (Found: C, 37.5; H, 3.5. $C_7H_8Cl_2O_2S$ requires C, 37.5; H, 3.5%); ν_{max}/cm^{-1} 1310, 1253, 1225, 1148, 1111, 938, 875, 821, 792 and 730; δ_H 5.89 (1 H, d, *J* 2, 6-H), 4.74 (1 H, s, 8-H), 3.80 (1 H, m, 5-H) and 3.46–2.77 (5 H, m, 1,2,4-H); δ_C 135.5 (=CCl), 131.4 (=CH), 68.2 (CHCl), 52.6, 51.9, 46.7 and 41.9; *m*/*z* 230/228/226 (M^+, 2/11/16%), 193/191 ($M^+ - Cl$, 2/5), 163 (11), 161 (19), 127/125 (34/100) and 91 (73).

Alternatively **11** could be obtained by reaction with dichlorocarbene under phase-transfer conditions.[12] A solution of the alkene **3** (216 mg, 1.5 mmol) and benzyltriethylammonium chloride (50 mg) in chloroform (5 cm^3) was stirred with 50% aqueous sodium hydroxide (10 cm^3) at 50 °C for 4 h. Ice (15 g) was added and the mixture extracted with CH_2Cl_2 (4 × 25 cm^3). Drying and evaporation of the extract followed by preparative TLC (silica, CH_2Cl_2) gave unreacted **3** (150 mg) and oily crystals (25 mg) which consisted of a 1:1 mixture of *7,7-dichloro-3-thiatricyclo[3.3.0.0^{6,8}]octane 3,3-dioxide* **10**; δ_H 3.7–2.7 (6 H, m, 1,2,4,5-H) and 1.29–1.18 (2 H, m, 6,8-H), and the rearranged isomer **11**. Recrystallisation from diethyl ether gave only **11** (15 mg, 4.4%) (14% on reacted **3**) with properties identical to those above.

Flash vacuum pyrolysis of 3 and 5–9

This was carried out using the equipment described previously[6] at pressures in the range 10^{-3}–10^{-2} Torr. After the pyrolysis the products were dissolved out of the cold trap in $CDCl_3$ for direct NMR spectroscopic analysis or in CH_2Cl_2 for purification by normal methods.

FVP of the alkene **3** (50 mg) at 500 °C gave entirely cyclohexa-1,3-diene **13**; δ_H 5.9–5.75 (4 H, m, 1,2,3,4-H) and 2.14 (4 H, m, 5,6-H).

FVP of **3** at 400 °C resulted in only partial reaction with some of the starting material recovered. The hydrocarbon products were *Z*-hexa-1,3-5-triene **12**; δ_H 6.9–6.6 (2 H, m, 2,5-H), 6.0–5.8 (2 H, m, 3,4-H) and 5.3–5.0 (4 H, m, 1,6-H) (good agreement with lit. spectrum[13]) and cyclohexa-1,3-diene **13**; δ_H as above, in a ratio of 1:3.

Using the method of Gaoni,[14] the alkene **3** (200 mg, 1.4 mmol) was added in portions to a boiling suspension of lithium aluminium hydride (200 mg, 5.4 mmol) in diethyl ether (50 cm^3). After heating under reflux for 1 h, a sample of the solution was withdrawn and analysed by GC. By comparison with a sample prepared using the literature method,[15] the products were shown to be *E*- and *Z*-hexa-1,3,5-triene **14** and **12** in a 1:1 ratio. The fact that the *E* and *Z* isomers do not interconvert under the conditions used was demonstrated by boiling a solution of *E*- and *Z*-hexa-1,3,5-triene in diethyl ether with $LiAlH_4$ for 1 h. Analysis by GC showed that the isomer ratio was unchanged.

FVP of the epoxide **5** (50 mg) at 580 °C gave *4,5-dihydrooxepine* **16** (30 mg, 55%) as a colourless liquid; δ_H 6.10 (2 H, d, *J* 7.5, 2,7-H), 5.20 (2 H, m, 3,6-H) and 2.30 (4 H, m, 4,5-H); δ_C 142.8, 108.5 and 26.9 (excellent agreement with literature data[16]).

FVP of aziridine **6** (60 mg) at 550 °C through a furnace packed with silica rods gave a brown oil which was purified by preparative TLC (silica, diethyl ether) to give *1-methoxycarbonyl-4,5-dihydroazepine* **17** as a colourless liquid (6 mg, 14%) (HRMS: found M^+, 153.0781. $C_8H_{11}NO_2$ requires *M*, 153.0790); ν_{max}/cm^{-1} ($CDCl_3$) 1704, 1450, 1380, 1317, 1232 and 1198; δ_H 6.65 (2 H, d, *J* 10, 2,7-H), 5.2–5.0 (2 H, m, 3,6-H), 3.79 (3 H, s, OMe) and 2.30 (4 H, m, 4,5-H); *m*/*z* 153 (M^+, 100%), 138 (20), 126 (22), 114 (32), 94 (53) and 79 (32).

FVP of aziridine **7** (85 mg) at 575 °C through a furnace packed with silica rods gave a brown oil which was purified by preparative TLC (silica, diethyl ether–petroleum, 1:1) to give *1-ethoxycarbonyl-4,5-dihydroazepine* **18** as a colourless liquid (6 mg, 10%) (HRMS: found M^+, 167.0943. $C_9H_{13}NO_2$ requires *M*, 167.0946); ν_{max}cm^{-1} ($CDCl_3$) 1715, 1367, 1323, 1224, 1190 and 1144; δ_H 6.67 (2 H, d, *J* 10, 2,7-H), 5.10 (2 H, m, 3,6-H), 4.23 (2 H, q, *J* 7, OCH_2), 2.30 (4 H, m, 4,5-H) and 1.31 (3 H, t, *J* 7, CH_3); *m*/*z* 167 (M^+, 100%), 149 (23), 105 (44) and 94 (90).

FVP of **8** (40 mg) at 475 °C gave a yellow oil which was shown by ^{1}H NMR and GCMS to consist of ten hydrocarbons. The largest component was cyclohepta-1,4-diene **19** (27% yield from **8**); δ_H 5.75–5.6 (4 H, m, 1,2,4,5-H), 2.85 (2 H, m, 3-H) and 2.24 (4 H, m, 6,7-H), whose identity was confirmed by comparison with an authentic sample,[17] and this was accompanied by seven other isomers of C_7H_{10} (39%) and two of C_7H_8 (6%).

FVP of **9** (17 mg) at 475 °C gave a colourless liquid which consisted mainly of cyclohepta-1,4-diene **19** (80%) confirmed by comparison with an authentic sample.

1,3-Dipolar cycloaddition to 3

5-Phenyl-3-oxa-9-thia-4-azatricyclo[5.3.0.0^{2,6}]dec-4-ene 9,9-dioxide 20. A solution of the alkene **3** (1.1 g, 7.6 mmol) and *N*-hydroxybenzimidoyl chloride (1.19 g, 7.6 mmol) in dry toluene (100 cm^3) was heated under reflux for 64 h. Evaporation followed by chromatography (alumina, petroleum–CH_2Cl_2) and recrystallisation from ethanol gave the *title compound* **20** (0.37 g, 19%) as colourless crystals, mp 175–176 °C (Found: C, 59.15; H, 5.0; N, 5.1. $C_{13}H_{13}NO_3S$ requires C, 59.3; H, 5.0; N, 5.3%); ν_{max}/cm^{-1} 1308, 1128, 878, 768, 691 and 666; δ_H 7.6–7.4 (5 H, m, Ph), 5.20 (1 H, dd, *J* 7.5, 2.5, 2-H), 4.4–4.2 (1 H, m, 6-H) and 3.5–3.2 (6 H, m, 1,7,8,10-H); δ_C (CD_3SOCD_3) see Table 1; *m*/*z* 263 (M^+, 9%), 145 (100), 144 (57), 117 (13) and 77 (22).

5-(4-Methoxyphenyl)-3-oxa-9-thia-4-azatricyclo[5.3.0.0^{2,6}]-dec-4-ene 9,9-dioxide 21. A solution of the alkene **3** (260 mg, 1.8 mmol) and *N*-hydroxy-4-methoxybenzimidoyl chloride (310 mg, 1.8 mmol) in dry toluene (20 cm^3) was heated under reflux for 48 h. Evaporation and recrystallisation of the residue from ethanol gave the *title compound* **21** (0.24 g, 45%) as colourless crystals, mp 182–184 °C (Found: C, 57.1; H, 5.15; N, 4.7. $C_{14}H_{15}NO_4S$ requires C, 57.3; H, 5.2; N, 4.8%); ν_{max}/cm^{-1} 1302, 1246, 1125, 872 and 835; δ_H 7.60 and 6.80 (4 H, AB pattern, *J* 10, Ar), 5.20 (1 H, dd, *J* 8, 4, 2-H), 4.30 (1 H, d, *J* 8, 6-H), 3.80 (3 H, s, OMe) and 3.6–3.1 (6 H, m, 1,7,8,10-H); δ_C see Table 1; *m*/*z* 293 (M^+, 30%) and 175 (100).

4,5-Diphenyl-3-oxa-9-thia-4-azatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide 22. A solution of the alkene **3** (150 mg, 1.04 mmol) and *N*-phenylbenzylideneamine *N*-oxide[19] in dry toluene (10 cm^3) was heated under reflux for 72 h. Evaporation followed by recrystallisation of the residue from ethanol gave the *title compound* **22** (0.10 g, 28%) as light brown crystals, mp 185–186 °C (Found: C, 66.6; H, 5.65; N, 3.95. $C_{19}H_{19}NO_3S$ requires C, 66.8; H, 5.6; N, 4.1%); ν_{max}/cm^{-1} 1598, 1490, 1309, 1132, 768, 742, 709 and 701; δ_H 7.5–7.0 (10 H, m, Ph), 4.80 (1 H, dd, *J* 7, 2, 2-H), 4.50 (1 H, d, *J* 7, 5-H) and 3.5–2.6 (7 H, m, 1,6,7,8,10-H); *m*/*z* 341 (M^+, 50%), 180 (17), 91 (100) and 77 (36).

Formation of other tricyclo[5.3.0.0^{2,6}] systems

8,10-Dioxo-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide 25. A solution of 2,5-dihydrothiophene 1,1-dioxide (1.25 g, 10.6 mmol) and maleimide (1.0 g, 10.3 mmol) in acetone (12 cm^3) was irradiated using a 400 W medium-pressure mercury lamp for 18 h. The resulting precipitate was filtered off and washed with acetone to give the title imide **25** (1.01 g, 46%) as colourless crystals, mp 342–346 °C (lit.,[4] 345 °C).

The same product could alternatively be prepared by reaction of the anhydride **1** with aqueous ammonia solution followed by vacuum sublimation to afford a product identical to that above (50%).

9-Methyl-8,10-dioxo-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide 26. To a suspension of the anhydride **1** (50.0 g, 230 mmol) in methanol (300 cm^3) was added 25% aqueous methylamine solution (135 cm^3, 340 mmol). The solution was stirred for 3 h and then evaporated. Recrystallisation of the residue from ethanol–water (10 : 1) gave the crude monomethylamide (44.1 g, 77%) as colourless crystals, mp 121–123 °C; ν_{max}/cm^{-1} 1640, 1570 and 1140; δ_H 8.0 (1 H, br s), 3.4–2.9 (8 H, m) and 3.15 (3 H, s); δ_C 175.7, 172.7, 54.6, 54.1, 46.4, 45.3, 34.4, 32.4 and 24.4.

A solution of this product (30.0 g, 120 mmol) and sodium acetate (3 g) in acetic anhydride (110 cm^3) was heated at 100 °C with stirring for 4 h. The mixture was left to cool for 12 h and the resulting precipitate was filtered off and washed with methanol (50 cm^3) and diethyl ether (50 cm^3) to give the *title imide* **26** (26.8 g, 96%) as colourless crystals, mp 235–237 °C (Found: C, 47.4; H, 4.8; N, 6.1. $C_9H_{11}NO_4S$ requires C, 47.2; H, 4.8; N, 6.1%); ν_{max}/cm^{-1} 1694, 1433, 1390, 1283, 1160, 1137, 1100, 959, 753 and 745; δ_H 3.40 (2 H, s, 1,7-H), 3.26 (6 H, s, 2,3,5,6-H) and 3.04 (3 H, s, Me); δ_C (CD_3SOCD_3) see Table 1; *m*/*z* 229 (M$^+$, 35%), 165 (58), 98 (20), 80 (100) and 79 (100).

8,10-Dioxo-9-phenyl-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide 27. A suspension of the anhydride **1** (20.0 g, 93 mmol) and aniline (8.4 cm^3, 8.6 g, 93 mmol) in methanol (250 cm^3) was stirred for 3 h. The resulting solid was filtered off and dried to give the crude monoanilide (20.2 g, 58%), mp 217–220 °C (lit.,[4] 220 °C).

A solution of this product (6.3 g, 20.3 mmol) and sodium acetate (0.6 g) in acetic anhydride (30 cm^3) was heated at 100 °C with stirring for 4 h. The resulting precipitate was filtered off and washed with methanol to give the *title imide* **27** (5.0 g, 84%) as colourless crystals, mp 308–314 °C (lit.,[4] 310–315 °C); δ_H (CF_3CO_2H) 7.6–7.5 (3 H, m), 7.15 (2 H, m) and 3.9–3.5 (8 H, m); δ_C (CD_3SOCD_3) see Table 1; *m*/*z* 291 (M$^+$, 69%), 119 (11) and 80 (100).

Dimethyl 3,3-dioxo-3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylate 28. A solution of the anhydride **1** (15.0 g, 69 mmol) in methanol (150 cm^3) containing concentrated sulfuric acid (0.5 cm^3) was heated under reflux for 3 h. The solution was cooled and the resulting precipitate filtered off and dried to give the *title diester* **28** (16.4 g, 90%) as colourless crystals, mp 126–127 °C (lit.,[4] 126–127 °C); δ_H 3.70 (6 H, s, OMe), 3.60 (4 H, m, 1,5,6,7-H) and 3.2–3.1 (4 H, m, 2,4-H); δ_C (CD_3SOCD_3) see Table 1; *m*/*z* 262 (M$^+$, 1%), 231 (62), 138 (66) and 99 (100).

8,11-Dioxo-4-thia-9,10-diazatricyclo[5.4.0.0^{2,6}]undecane 4,4-dioxide 29. A solution of the dimethyl ester **28** (1.30 g, 4.96 mmol) and hydrazine hydrate (4 cm^3) in methanol (20 cm^3) was heated under reflux for 2 h. The precipitate formed upon cooling was filtered off and washed with methanol to afford 6,7-di(hydrazidocarbonyl)-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (1.25 g, 79%), mp 239–241 °C.

A sample of the dihydrazide (0.53 g) was sublimed at 220 °C and 10^{-2} Torr to afford the *title compound* **29** (0.49 g, 49%) as pale yellow crystals, mp 226–232 °C (lit.,[4] 228–230 °C).

6,7-Bis(hydroxymethyl)-3-thiabicyclo[3.2.0]heptane 3,3-dioxide 30. A solution of the above diester (10.0 g, 38 mmol) in dry THF (50 cm^3) was added over 30 min to a stirred suspension of lithium aluminium hydride (5.80 g, 150 mmol) in dry THF (120 cm^3). The mixture was stirred for 1 h at room temperature and then heated under reflux for 1 h. After cooling, the excess of lithium aluminium hydride was destroyed by dropwise addition of water (7 cm^3), 2 M sodium hydroxide solution (7 cm^3) and finally water (21 cm^3). The mixture was filtered and the filtrate evaporated to give the first batch of product. Soxhlet extraction of the inorganic solids using THF (500 cm^3) for 48 h followed by evaporation afforded a further batch of product. These were combined and recrystallised from THF to give the *title diol* **30** (5.4 g, 69%) as colourless crystals, mp 98–100 °C (lit.,[4] 75–82 °C) (Found: C, 46.6; H, 6.8. $C_8H_{14}O_4S$ requires C, 46.6; H, 6.8%); ν_{max}/cm^{-1} 3500–3100, 1310, 1255, 1150 and 1050; δ_H (CF_3CO_2H) 4.75–4.65 (2 H, m, OH), 4.14–4.04 (4 H, m, C*H*$_2$OH) and 3.5–2.9 (8 H, m); δ_C (CD_3SOCD_3) see Table 1; *m*/*z* 170 (M$^+$, 7%), 79 (79) and 70 (100).

4-Oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide 33. A solution of the diol **30** (1.0 g, 4.9 mmol) in acetone (50 cm^3) containing concentrated sulfuric acid (0.5 cm^3) was heated under reflux for 48 h. Evaporation gave a brown oil which was purified by chomatography on silica (CH_2Cl_2–acetone, 5 : 1) to give the *title compound* **33** (0.50 g, 55%) as colourless crystals, mp 129–130 °C (Found: C, 50.8; H, 6.2. $C_8H_{12}O_3S$ requires C, 51.0; H, 6.4%); ν_{max} 1302, 1287, 1179, 1134, 1107, 1073 and 690; δ_H 3.90 (2 H, d, *J* 9, 3,5-H), 3.45 (2 H, dd, *J* 9, 4, 3,5-H), 3.10 (4 H, m, 1,2,6,7-H), 2.90 (2 H, m, 8,10-H) and 2.80 (2 H, m, 8,10-H); δ_C see Table 1; *m*/*z* 188 (M$^+$, 8%), 94 (60), 79 (100) and 54 (78).

Alternatively a solution of toluene-4-sulfonyl chloride (1.50 g, 8 mmol) and the diol **30** (1.50 g, 7 mmol) in dry pyridine (12 cm^3) was stirred at room temperature for 18 h and then heated at 100 °C for 1 h. The solution was added to ice (50 g) and the resulting mixture neutralised with 2 M hydrochloric acid and then extracted with CH_2Cl_2 (3 × 100 cm^3). Drying and evaporation of the extracts followed by chromatography of the residue and recrystallisation from CH_2Cl_2–hexane (1 : 1) gave **33** (0.34 g, 26%) identical in all respects to the material above.

6,7-Bis(methylsulfonyloxymethyl)-3-thiabicyclo[3.2.0]heptane 3,3-dioxide 31. A solution of the diol **30** (6.54 g, 31.7 mmol) in dry pyridine (25 cm^3) was added dropwise to a stirred solution of methanesulfonyl chloride (11.1 g, 97 mmol) in dry pyridine (120 cm^3) cooled in an ice–salt bath such that the temperature remained below 0 °C. After the addition the mixture was stirred at −5–0 °C for 2 h and then cold 1 M hydrochloric acid (200 cm^3) was added slowly such that the temperature did not exceed 20 °C. The resulting solid was filtered off and washed with 1 M hydrochloric acid (100 cm^3) and water (200 cm^3) and then recrystallised from ethanol–water (10 : 1) to give the *title compound* **31** (8.65 g, 75%) as colourless crystals, mp 190–192 °C (Found: C, 33.2; H, 5.1. $C_{10}H_{18}O_8S_3$ requires C, 33.1; H, 5.0%); ν_{max}/cm^{-1} 1333, 1295, 1175, 1141, 1105, 980, 858, 833 and 750; δ_H (CD_3SOCD_3) 4.4–4.3 (4 H, m, C*H*$_2$O) and 3.2–2.8 (14 H, m); δ_C (CD_3SOCD_3) see Table 1.

4,9-Dithiatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide 34. A solution of the dimesylate **31** (5.0 g, 13.8 mmol) and sodium sulfide nonahydrate (9.92 g, 41.4 mmol) in ethanol (75 cm^3) and water (75 cm^3) was heated under reflux for 4 h. The solution was partially evaporated to remove the ethanol and the aqueous residue extracted with CH_2Cl_2 (2 × 100 cm^3). Drying and evaporation followed by reprecipitation from chloroform by addition to petroleum (bp 40–60 °C) gave the *title compound* **34** (1.73 g, 62%) as colourless crystals, mp 195–196 °C (Found: C, 47.3; H, 6.0. $C_8H_{12}O_2S_2$ requires C, 47.0; H, 5.9%); ν_{max}/cm^{-1} 1290, 1235, 1190, 1130, 1090, 905 and 687; δ_H 3.2–2.9 (6 H, m, 2,3,5,6-H) and 2.9–2.5 (6 H, m, 1,7,8,10-H); δ_C see Table 1; *m*/*z* 204 (M$^+$, 47%), 86 (100) and 85 (94).

6,7-Bis(4-tolylsulfonyloxymethyl)-3-thiabicyclo[3.2.0]heptane 3,3-dioxide 32. A solution of the diol **30** (5.0 g, 24.3 mmol) in dry pyridine (40 cm^3) was added dropwise to a suspension of toluene-4-sulfonyl chloride (29.7 g, 156 mmol) in dry pyridine (40 cm^3) stirred at 0 °C. The mixture was stirred at 0 °C for 3 h and then added to water (300 cm^3). The resulting precipitate was filtered off, washed with water (100 cm^3) and recrystallised from ethanol to give the *title compound* **32** (6.39 g, 51%) as colourless needles, mp 127–128 °C (Found: C, 51.1; H, 5.0. $C_{22}H_{26}O_8S_3$ requires C, 51.3; H, 5.1%); ν_{max}/cm^{-1} 1600, 1315,

1175, 1097, 956, 899, 858, 812, 696 and 668; δ_H 7.70 and 7.40 (8 H, AB pattern, *J* 8, Ar), 4.15–4.05 (4 H, m, C*H*$_2$O), 3.1–2.8 (8 H, m) and 2.46 (6 H, s, Me); δ_C see Table 1; *m*/*z* 514 (M^+, 0.2%), 343 (14), 172 (36), 155 (100), 124 (4) and 91 (100).

9-Benzyl-4-thia-9-azatricyclo[5.3.0.0^{2,6}]decane 4,4-dioxide 36. A solution of the ditosylate **32** (5.0 g, 9.73 mmol) and benzylamine (3.1 g, 29 mmol) in ethanol (50 cm^3) was heated under reflux for 48 h. The mixture was evaporated and the residual solid extracted with CH_2Cl_2 (100 cm^3). The extract was filtered and evaporated and the residue recrystallised from ethanol to give the *title compound* **36** as colourless crystals, mp 132–135 °C (Found: C, 64.8; H, 6.6; N, 5.0. $C_{15}H_{19}NO_2S$ requires C, 64.9; H, 6.9; N, 5.0%); ν_{max}/cm^{-1} 2780, 1603, 1300, 1247, 1140, 740 and 700; δ_H 7.4–7.2 (5 H, m, Ph), 3.65 (2 H, s, C*H*$_2$Ph), 3.1–2.6 (10 H, m) and 2.2–2.0 (2 H, m, 1,7-H); δ_C see Table 1; *m*/*z* 277 (M^+, 47%), 200 (26), 186 (47) and 91 (100).

9-Phenyl-4-thia-9-azatricyclo5.3.0.0^{2,6}]decane 4,4-dioxide 35. The imide **27** (4.5 g, 15.5 mmol) was added over 15 min to a stirred suspension of lithium aluminium hydride (1.40 g, 36.2 mmol) in dry THF (100 cm^3). The mixture was heated under reflux for 5 h. The excess of lithium aluminium hydride was destroyed by dropwise addition of water (2 cm^3) in THF (20 cm^3), 4 M sodium hydroxide solution (2 cm^3) and finally water (6 cm^3). The mixture was filtered and the filtrate evaporated. The residue was extracted with CH_2Cl_2 (100 cm^3) which was dried and evaporated. Chromatography of the residue on silica (CH_2Cl_2) followed by recrystallisation from ethanol gave the *title compound* **35** (0.13 g, 3%) as brown crystals, mp 200–204 °C (Found: C, 63.6; H, 6.65; N, 5.15. $C_{14}H_{17}NO_2S$ requires C, 63.8; H, 6.5; N, 5.3%); ν_{max}/cm^{-1} 1602, 1302, 1141, 760 and 695; δ_H 7.5–7.25 (2 H, m, Ph), 6.9–6.7 (3 H, m, Ph), 3.8–3.5 (4 H, m, 8,10-H) and 3.2–2.9 (8 H, m); *m*/*z* 263 (M^+, 100%), 144 (14), 119 (33) and 91 (57).

Pyrolysis of tricyclo[5.3.0.0^{2,6}] systems

FVP of **20** (50 mg) at 500 °C followed by microdistillation of the product gave *cis-4,5-dihydro-3-phenyl-4,5-divinylisoxazole* **23** (7.0 mg, 19%) as a colourless liquid, bp 100 °C/0.1 Torr (Found: C, 78.1; H, 6.4; N, 7.3. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%); ν_{max}/cm^{-1} 1447, 1346, 987, 926, 767 and 693; δ_H 7.74–7.64 (2 H, m, Ph), 7.4–7.2 (3 H, m, Ph), 6.1–4.95 (7 H, m, vinyl and 5-H) and 4.14 (1 H, d, *J* 10, 4-H); *m*/*z* 199 (M^+, 15%), 143 (100), 117 (70) and 115 (25).

FVP of **21** (50 mg) at 500 °C followed by vacuum sublimation of the product (100 °C/5 × 10^{-3} Torr) gave *cis-4,5-dihydro-3-(4-methoxyphenyl)-4,5-divinylisoxazole* **24** (13 mg, 33%) as colourless crystals, mp 58–60 °C (Found: C, 73.2; H, 6.5; N, 6.0. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.6; N, 6.1%); ν_{max}/cm^{-1} 1607, 1512, 1245, 1177, 1043, 837 and 810; δ_H 7.70 and 6.90 (4 H, AB pattern, *J* 10, Ar), 6.1–4.9 (6 H, m, vinyl), 4.10 (1 H, m, 5-H), 3.66 (3 H, s, Me) and 3.20 (1 H, m, 4-H); δ_C see Table 2; *m*/*z* 229 (M^+, 100%) and 173 (92).

FVP of anhydride **1** (15.0 g, 69 mmol) at 630 °C followed by Kugelrohr distillation of the product gave *cis-1,2-divinylsuccinic anhydride* **37** (8.43 g, 80%) as a colourless liquid, bp (oven temp.) 65 °C/10 Torr (Found: C, 62.9; H, 5.45. $C_8H_8O_3$ requires C, 63.1; H, 5.3%); n_D^{25} 1.4835; ν_{max}/cm^{-1} 1900–1700, 1642, 1417, 1206, 1072, 945 and 783; δ_H 5.9–5.5 (2 H, m, =CH), 5.4–5.3 (4 H, m, =CH$_2$), 3.9–3.4 (2 H, dd, *J* 4.5, 2, 1,2-H); δ_C see Table 2; *m*/*z* 152 (M^+, 11%), 108 (7), 80 (100) and 79 (100).

FVP of **25** (353 mg) at 650 °C followed by recrystallisation of the product from chloroform–petroleum (bp 60–68 °C) (1 : 3) gave *cis-1,2-divinylsuccinimide* **38** (157 mg, 63%) as colourless crystals, mp 108–110 °C (Found: C, 63.6; H, 5.9; N, 9.0. $C_8H_9NO_2$ requires C, 63.6; H, 6.0; N, 9.3%); ν_{max}/cm^{-1} 3195, 1781, 1700, 1640, 1275, 1192, 1151, 990 and 944; δ_H 8.65–8.35 (1 H, br s, NH), 5.92–5.26 (6 H, m, vinyl) and 3.70 (2 H, dd, *J* 5, 2, 1,2-H); *m*/*z* 151 (M^+, 4%), 123 (1), 108 (8), 80 (100), 79 (91) and 27 (18).

FVP of **26** (1.0 g) at 625 °C followed by microdistillation of the product gave *cis-N-methyl-1,2-divinylsuccinimide* **39** (0.32 g, 58%) as a pale yellow oil, bp 100 °C/10^{-3} Torr (Found: C, 65.3; H, 6.8; N, 8.65%; M^+, 165.0778. $C_9H_{11}NO_2$ requires C, 65.4; H, 6.7; N, 8.5%; *M*, 165.0790); n_D^{19} 1.486; ν_{max}/cm^{-1} 1690, 1435, 1380, 1290, 980 and 930; δ_H 6.1–5.2 (6 H, m, vinyl), 3.8–3.6 (2 H, m, 1,2-H) and 3.05 (3 H, s, Me); δ_C see Table 2; *m*/*z* 165 (M^+, 78%), 80 (100), 79 (100), 64 (88) and 60 (55).

FVP of **27** (283 mg) at 625 °C gave a solid which was dissolved in chloroform and the solution filtered. Evaporation followed by recrystallisation of the residue from ethanol gave *cis-N-phenyl-1,2-divinylsuccinimide* **40** (120 mg, 52%) as colourless needles, mp 134–136 °C (Found: C, 73.7; H, 5.8; N, 6.1. $C_{14}H_{13}NO_2$ requires C, 74.0; H, 5.8; N, 6.2%); ν_{max}/cm^{-1} 1767, 1598, 1496, 1264, 1188, 933, 753 and 692; δ_H 7.5–7.2 (5 H, m, Ph), 5.95–5.28 (6 H, m, vinyl) and 3.75 (2 H, dd, *J* 7, 2, 1,2-H); δ_C see Table 2; *m*/*z* 227 (M^+, 62%), 157 (5), 119 (8), 108 (8), 91 (8), 80 (100) and 79 (60).

FVP of **33** (486 mg) at 625 °C followed by microdistillation of the product gave *cis-3,4-divinyltetrahydrofuran* **41** (197 mg, 62%) as a colourless liquid, bp 41 °C/41 Torr (Found: C, 41.0; H, 4.3. $C_8H_{12}O$ requires C, 41.1; H, 4.6%); n_D^{18} 1.465; ν_{max}cm^{-1} 1638, 1423, 1047, 991 and 910; δ_H 5.9–5.6 (2 H, m, =CH), 5.1–5.0 (4 H, m, =CH$_2$), 3.95 (2 H, dd, *J* 8.5, 7, 2,5-H), 3.65 (2 H, dd, *J* 8.5, 6, 2,5-H) and 3.1–2.8 (2 H, m, 3,4-H); δ_C see Table 2; *m*/*z* 124 (M^+, 1%), 94 (45), 79 (100), 77 (38) and 54 (43).

FVP of **34** (320 mg) at 620 °C followed by microdistillation of the product gave *cis-3,4-divinyltetrahydrothiophene* **42** (27 mg, 25%) as a colourless liquid, bp 140 °C/16 Torr (Found: C, 68.7; H, 8.6. $C_8H_{12}S$ requires C, 68.5; H, 8.6%); ν_{max}/cm^{-1} 1640, 1450, 1425, 980 and 917; δ_H 6.0–5.0 (6 H, m, vinyl) and 3.1–2.6 (6 H, m, 2,3,4,5-H); δ_C see Table 2; *m*/*z* 140 (M^+, 30%), 86 (100) and 85 (76).

FVP of **35** (60 mg) at 625 °C resulted largely in decomposition of the starting material in the inlet tube and only a very small amount of product was obtained. Analysis of this by ^{1}H NMR showed that it was mainly the expected *cis-1-phenyl-3,4-divinylpyrrolidine* **43**; δ_H 7.45–7.25 (2 H, m, Ph), 6.8–6.5 (3 H, m, Ph), 6.2–4.9 (6 H, m, vinyl) and 3.5–2.9 (6 H, m, 2,3,4,5-H), but no further characterisation was possible.

FVP of **36** (90 mg) at 525 °C followed by microdistillation of the product gave *cis-1-benzyl-3,4-divinylpyrrolidine* **44** (40 mg, 58%) as a light brown oil, bp 100 °C/10^{-3} Torr (Found: C, 84.6; H, 9.1; N, 6.7%; M^+, 213.1516. $C_{15}H_{19}N$ requires C, 84.5; H, 9.0; N, 6.6%; *M*, 213.1517); ν_{max}/cm^{-1} 1642, 1454, 912, 802, 742 and 700; δ_H 7.4–7.2 (5 H, m, Ph), 6.1–5.8 (6 H, m, vinyl), 3.60 (2 H, s, C*H*$_2$Ph), 3.1–2.9 (4 H, m, 2,5-H) and 2.4–2.1 (2 H, m, 3,4-H); *m*/*z* 213 (M^+, 33%), 133 (29), 91 (86) and 42 (100).

FVP of **29** (476 mg) at 600 °C followed by vacuum sublimation of the product gave *cis-4,5-divinylhexahydropyridazine-3,6-dione* **47** (280 mg, 68%) as colourless plates, mp 65–67 °C (Found: C, 57.6; H, 6.0; N, 16.7. $C_8H_{10}N_2O_2$ requires C, 57.8; H, 6.1; N, 16.9%); ν_{max}/cm^{-1} 3350–3180, 3090, 1790, 1710, 1640, 1205, 992, 925, 879 and 802; δ_H (CD_3SOCD_3) 5.85–5.5 (2 H, m, =CH), 5.35–5.15 (4 H, m, =CH$_2$), 4.70 (2 H, br s, NH) and 3.71 (2 H, dd, *J* 5, 2, 4,5-H); δ_C (CD_3SOCD_3) see Table 2; *m*/*z* 166 (M^+, 96%), 150 (10), 137 (10), 107 (22), 80 (77), 79 (100) and 70 (53).

Alternative synthesis of 41 from 37

A mixture of the anhydride **37** (8.43 g, 55 mmol) and sulfuric acid (0.5 cm^3) in methanol (130 cm^3) was heated under reflux for 24 h. The solution was filtered and the filtrate evaporated. The resulting oil crystallised with time and was recrystallised from petroleum to give *dimethyl* (*meso*)*-hexa-1,5-diene-3,4-dicarboxylate* **45** (5.6 g, 51%) as colourless crystals, mp 36–37 °C (Found: C, 60.45; H, 6.9. $C_{10}H_{14}O_4$ requires C, 60.6; H,

7.1%); ν_{max}/cm^{-1} 1743, 1640, 1315, 1235, 1088, 1000, 892, 787 and 695; δ_H 5.9–5.6 (2 H, m, 2,5-H), 5.3–5.1 (4 H, m, 1,6-H), 3.62 (6 H, s, OMe) and 3.45 (2 H, dd, *J* 6, 2, 3,4-H); δ_C see Table 2; *m*/*z* 198 (M$^+$, 1%), 167 (18), 139 (23), 138 (27) and 99 (100).

A solution of the diester **45** (10.76 g, 54 mmol) in dry THF (50 cm^3) was added dropwise over 30 min to a stirred suspension of lithium aluminium hydride (8.26 g, 220 mmol) in dry THF (170 cm^3). The mixture was then stirred for 1 h at room temperature and heated under reflux for 1 h. After cooling, water (8 cm^3) was cautiously added followed by 4 M sodium hydroxide solution (8 cm^3) and then water (24 cm^3). The mixture was filtered and the filtrate evaporated. The residue was taken up in CH_2Cl_2 (100 cm^3) which was washed with water, dried and evaporated. Kugelrohr distillation of the resulting oil gave (*meso*)-*3,4-di(hydroxymethyl)hexa-1,5-diene* **46** (6.7 g, 87%) as a colourless oil, bp (oven temp.) 100 °C/0.8 Torr (Found: C, 67.45; H, 10.1. $C_8H_{14}O_2$ requires C, 67.5; H, 9.9%); n_D^{18} 1.4865; ν_{max}/cm^{-1} 3700–3100, 1640, 1425, 1055, 995 and 917; δ_H 5.9–5.5 (2 H, m, 2,5-H), 5.2–5.0 (4 H, m, 1,6-H), 3.8–3.4 (4 H, m, C*H*$_2$OH) and 2.5–2.1 (4H, m, 3,4-H and OH); δ_C see Table 2; *m*/*z* 142 (M$^+$, 0.3%), 124 (1), 94 (45), 79 (75) and 54 (100).

A solution of the diol **46** (3.8 g, 27 mmol) and toluene-4-sulfonic acid (0.30 g, 1.6 mmol) in dry benzene (60 cm^3) was heated under reflux with a Dean and Stark trap for 40 h. The solution was evaporated and the residue distilled to give *cis-3,4-divinyltetrahydrofuran* **41** (2.03 g, 62%) as a colourless liquid, bp 41 °C/41 Torr which had spectroscopic properties identical to the material obtained from FVP of **33**.

Diels–Alder cycloaddition to 3

8,9,10,11-Tetrachloro-4-thiatricyclo[5.4.0.0^{2,6}]undeca-8,10-diene 4,4-dioxide 48. A solution of the alkene **3** (100 mg, 0.69 mmol) and tetrachlorothiophene 1,1-dioxide[18] (194 mg, 0.76 mmol) in dry benzene (10 cm^3) was heated under reflux for 48 h. Evaporation followed by preparative TLC (alumina, diethyl ether) and recrystallisation from chloroform–hexane (1 : 1) gave the *title adduct* **48** (78 mg, 34%) as colourless needles, mp 180–181 °C (Found: C, 36.1; H, 2.4%; M$^+$, 331.9012. $C_{10}H_8Cl_4O_2S$ requires C, 36.0; H, 2.4; *M*, 331.8999); ν_{max}/cm^{-1} 1617, 1319, 1305, 1233, 1207, 1143, 1101, 900, 750 and 719; δ_H 3.73 (2 H, m, 1,7-H), 3.55 (2 H, m, 2,6-H) and 3.18 (4 H, m, 3,5-H); *m*/*z* (^{35}Cl peaks only) 332 (M$^+$, 11%), 232 (7), 214 (tetrachlorobenzene, 100), 179 (9), 162 (10) and 54 (butadiene, 14).

1,9,10,11-Tetraphenyl-5-thia-12-oxotetracyclo[7.2.1.0^{2,8}.0^{3,7}]-dodec-10-ene 5,5-dioxide 49. A solution of the alkene **3** (0.45 g, 3.1 mmol) and tetraphenylcyclopentadienone (1.20 g, 3.1 mmol) in dry benzene (25 cm^3) was heated under reflux for 64 h. Evaporation followed by leaching of the residue with diethyl ether to remove unreacted diene and recrystallisation of the residue from benzene gave the *title adduct* **49** (0.87 g, 55%) as colourless needles, mp 156–157 °C (Found: C, 79.75; H, 5.55. $C_{35}H_{28}O_3S$ requires C, 79.5; H, 5.3%); ν_{max}/cm^{-1} 1780, 1610, 1315 and 1140; δ_H 7.46–6.46 (20 H, m, Ph), 3.50–3.41 (2 H, m, 2,6-H), 3.34–3.18 (4 H, m, 3,5-H) and 2.85–2.66 (2 H, m, 1,7-H); *m*/*z* 528 (M$^+$, 1%), 500 (12) and 382 (tetraphenylbenzene, 100).

1,9-Diphenyl-5-thia-16-oxapentacyclo[7.6.1.0^{2,8}.0^{3,7}.0^{10,15}]-hexadeca-10,12,14-triene 5,5-dioxide 50. A solution of the alkene **3** (348 mg, 2.42 mmol) and 1,3-diphenylisobenzofuran (656 mg, 2.43 mmol) in dry benzene (25 cm^3) was heated under reflux for 15 h. Evaporation followed by reprecipitation of the residue from chloroform by addition to hexane and recrystallisation from ethanol–CH_2Cl_2 (4 : 1) gave the *title adduct* **50** (254 mg, 25%) as colourless needles, mp 234–235 °C (Found: C, 75.1; H, 5.2. $C_{26}H_{22}O_3S$ requires C, 75.3; H, 5.4%); ν_{max}/cm^{-1} 1600, 1300 and 1140; δ_H 7.62–7.30 (10 H, m, Ph), 7.26–6.80 (4 H, m, Ar), 3.20–2.94 (6 H, m, 2,4,6,8-H) and 2.84–2.60 (2 H, m, 3,7-H); *m*/*z* 414 (M$^+$, 0.3%), 396 (8), 332 (5), 270 (diphenylisobenzofuran, 100), 241 (9), 165 (7), 105 (10) and 77 (12).

Pyrolysis of Diels–Alder adducts 48–50

FVP of the adduct **48** (25 mg) at 550 °C followed by preparative TLC of the product (alumina, diethyl ether) gave 1,2,3,4-tetrachlorobenzene (5 mg, 31%) as colourless crystals, mp 43–45 °C (lit.,[20] 45–46 °C); δ_H 7.23 (s). The product was identical to an authentic sample of tetrachlorobenzene by IR and GC.

FVP of the adduct **49** (0.57 g) at 330 °C followed by recrystallisation of the product from benzene gave *3,4,5,6-tetraphenyl-10-thiatetracyclo[6.3.0.0^{2,4}.0^{3,7}]undec-5-ene 10,10-dioxide* **51** (0.35 g, 65%) as colourless needles, mp 274–276 °C (Found: C, 81.85; H, 5.6. $C_{34}H_{28}O_2S$ requires C, 81.6; H, 5.6%); ν_{max}/cm^{-1} 1600, 1305 and 1125; δ_H 7.18–6.90 (20 H, m, Ph), 4.14 (1 H, s, 7-H), 3.63–3.50 (2 H, m, 1,8-H), 3.43–3.30 (1 H, m, 2-H) and 3.08–2.94 (4 H, m, 9,11-H); δ_C 138.9, 138.6, 137.5, 136.5, 136.0 and 135.3 (4 × C-1 of Ph and C=C), 129.8, 128.9, 128.8, 128.4, 128.2, 127.7, 127.6, 127.5, 127.0, 126.6, 126.4 and 126.1 (20 × aromatic CH), 62.5 (CH), 59.6 (4ry), 57.6 (4ry), 56.8 (CH$_2$), 53.9 (CH), 52.7 (CH$_2$), 40.0 (CH) and 38.3 (CH); *m*/*z* 500 (M$^+$, 40%) and 382 (tetraphenylbenzene, 100).

FVP of **49** (65 mg) at 675 °C followed by preparative TLC of the product (alumina, hexane–diethyl ether, 12 : 1) gave 1,2,3,4-tetraphenylbenzene (12 mg, 24%) identical with an authentic sample.

FVP of the adduct **50** (46 mg) at 525 °C gave 1,3-diphenylisobenzofuran (25 mg, 83%) as the only non-volatile product which was identified by ^{1}H NMR and TLC comparison with an authentic sample.

Synthesis and FVP of methylated anhydrides

1-Methyl-3,5-dioxo-4-oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide 52. A solution of 3-methyl-2,5-dihydrothiophene 1,1-dioxide (15.0 g, 114 mmol) and maleic anhydride (13.7 g, 140 mmol) in acetone (450 cm^3) was irradiated with a 400 W medium-pressure mercury lamp for 24 h. The mixture was evaporated and the residual oil triturated with chloroform to give the *title compound* **52** (9.42 g, 36%) as colourless crystals, mp 157–159 °C (Found: C, 46.8; H, 4.5. $C_9H_{10}O_5S$ requires C, 46.9; H, 4.4%); ν_{max}/cm^{-1} 1860, 1777, 1308, 1153, 1118, 1059, 905 and 723; δ_H (CD_3COCD_3) 3.85–3.10 (7 H, m) and 1.48 (3 H, s, Me); *m*/*z* 230 (M$^+$, 6%), 138 (31), 99 (90) and 93 (100).

2-Methyl-3,5-dioxo-4-oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide 54. A solution of 2,5-dihydrothiophene 1,1-dioxide (15.0 g, 127 mmol) and citraconic anhydride (17.1 g, 152 mmol) in acetone (300 cm^3) was irradiated with a 400 W medium-pressure mercury lamp for 24 h. The resulting precipitate was filtered off and washed with acetone to give the *title compound* **54** (13.1 g, 45%) as colourless crystals, mp 249–250 °C (Found: C, 47.1; H, 4.35. $C_9H_{10}O_5S$ requires C, 46.9; H, 4.4%); ν_{max}/cm^{-1} 1858, 1776, 1303, 1141, 1006, 920, 771, 721 and 680; δ_H (CD_3COCD_3) 3.76–3.30 (7 H, m) and 1.57 (3 H, s, Me); *m*/*z* 231 (M + H$^+$, 1%), 158 (29), 110 (10), 94 (41), 79 (100) and 77 (38).

FVP of **52** (1.285 g) at 580 °C followed by Kugelrohr distillation of the product gave *cis-1-isopropenyl-2-vinylsuccinic anhydride* **53** (0.64 g, 69%) as a colourless liquid, bp (oven temp.) 110 °C/0.3 Torr (HRMS: found M$^+$, 166.0641. $C_9H_{10}O_3$ requires *M*, 166.0630); ν_{max}/cm^{-1} 1865, 1785, 1650, 1455, 1445, 1423, 1386, 1033 and 977; δ_H 5.81–5.63 (1 H, m, vinyl), 5.52–5.39 (2 H, m, C(Me)=C*H*$_2$), 5.16–5.04 (2 H, m, vinyl), 4.0–3.87 (2 H, m, 1,2-H) and 1.73 (3 H, s, Me); δ_C see Table 2; *m*/*z* 166 (M$^+$, 14%), 122 (17), 94 (36) and 79 (100).

FVP of **54** (1.40 g) at 580 °C followed by Kugelrohr distillation of the product gave *cis-1-methyl-1,2-divinylsuccinic*

anhydride **55** (872 mg, 86%) as a colourless liquid, bp (oven temp.) 110–115 °C/0.8 Torr (HRMS: found M^+, 166.0628. $C_9H_{10}O_3$ requires *M*, 166.0630); ν_{max}/cm^{-1} 1850, 1790, 1674, 1642, 1454, 1416, 1380, 1235 and 939; δ_H 5.89–5.10 (6 H, m, vinyl), 3.51 (1 H, d, *J* 7, 2-H) and 1.49 (3 H, s, Me); δ_C see Table 2; *m*/*z* 166 (M^+, 0.5%), 122 (0.1), 94 (73), 79 (100) and 77 (41).

Acknowledgements

We thank British Petroleum Research International Ltd. for studentships (C. M. H. and S. J. W.).

References

1 R. A. Aitken, I. Gosney and J. I. G. Cadogan, *Prog. Heterocycl. Chem.*, 1992, **4**, 1.
2 R. A. Aitken, I. Gosney and J. I. G. Cadogan, *Prog. Heterocycl. Chem.*, 1993, **5**, 1.
3 Preliminary communications, J. I. G. Cadogan, I. Gosney, L. M. McLaughlin and B. J. Hamill, *J. Chem. Soc.*, *Chem. Commun.*, 1980, 1242; R. A. Aitken, J. I. G. Cadogan, I. Gosney, B. J. Hamill and L. M. McLaughlin, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 1164.
4 V. Sh. Shaikhrazieva, R. S. Enikeev and G. A. Tolstikov, *Zh. Org. Khim.*, 1972, **8**, 377.
5 C. W. Jefford, T. W. Wallace and M. Acar, *J. Org. Chem.*, 1977, **42**, 1654.
6 J. I. G. Cadogan, D. K. Cameron, I. Gosney, E. J. Tinley, S. J. Wyse and A. Amaro, *J. Chem. Soc.*, *Perkin Trans. 1*, 1991, 2081.
7 J. J. Bloomfield, D. C. Owsley and R. Srinivasan, *Org. Photochem. Synth.*, 1976, **2**, 36.
8 R. A. Aitken, I. Gosney, H. Farries, M. H. Palmer, I. Simpson, J. I. G. Cadogan and E. J. Tinley, *Tetrahedron*, 1984, **40**, 2487.
9 M. Seno, T. Namba and H. Kise, *J. Org. Chem.*, 1978, **43**, 3345.
10 R. C. De Selms and C. M. Combs, *J. Org. Chem.*, 1963, **28**, 2206.
11 D. Seyferth and R. L. Lambert, Jr., *J. Organomet. Chem.*, 1969, **16**, 21.
12 Y. Gaoni, *J. Org. Chem.*, 1981, **46**, 4502.
13 P. Albriktsen and R. K. Harris, *Acta Chem. Scand.*, 1973, **27**, 1875.
14 Y. Gaoni, *Tetrahedron Lett.*, 1977, 947.
15 J. C. H. Hwa, P. L. de Benneville and H. J. Sims, *J. Am. Chem. Soc.*, 1960, **82**, 2537.
16 J. C. Pommelet, N. Manisse and J. Chuche, *Tetrahedron*, 1972, **28**, 3929; H. Günther and G. Jikeli, *Chem. Ber.*, 1973, **106**, 1863.
17 G. R. Wiger and M. F. Rettig, *J. Am. Chem. Soc.*, 1976, **98**, 4168.
18 M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 856.
19 O. H. Wheeler and P. H. Gore, *J. Am. Chem. Soc.*, 1956, **78**, 3363.
20 F. Beilstein and A. Kurbatow, *Liebigs Ann. Chem.*, 1878, **192**, 228.

Paper 8/09326A