Preparation and Pyrolysis of some Bi- and Tri-cyclic Sulfones Derived from Photochemical [2+2] Cycloaddition of 2,3-Dihydrothiophene 1,1-Dioxide (2-Sulfolene)

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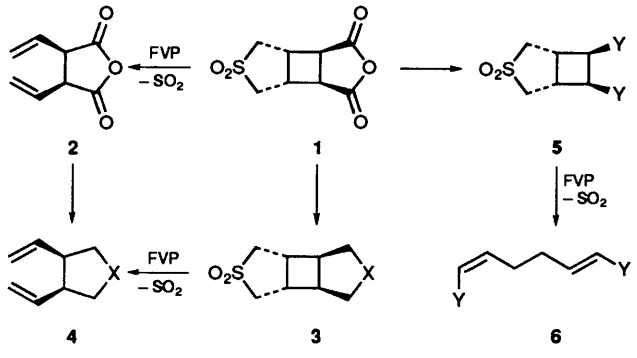
Photochemical reaction of 2,3-dihydrothiophene 1,1-dioxide [2-sulfolene] with maleic anhydride gives the [2 + 2] cycloadduct **8** and simple reactions of the anhydride function provide access to a wide range of new bi- and tri-cyclic sulfones **9–13** and **15–24** containing the novel 2-thiabicyclo[3.2.0]heptane 2,2-dioxide ring system. On pyrolysis these undergo either cycloreversion with elimination of 2-sulfolene or in one case extrusion of ethene and SO_2 to give the 1,3-diene. Oxidative bis-decarboxylation of the diacid from hydrolysis of **8** gives the new simple alkene sulfone **31**. Pyrolysis of this results in loss of only SO_2 to give cyclohexa-1,3-diene, but its epoxide **34** loses SO_2 and ethene to afford furan, thus making **31** a synthetic equivalent of cyclobutadiene.

Thermal extrusion of SO_2 from a wide variety of heterocyclic systems has recently formed the basis of numerous useful synthetic methods.[1] Some time ago we reported that the [2 + 2] cycloadduct **1** between 2,5-dihydrothiophene 1,1-dioxide ('3-sulfolene') and maleic anhydride, which was originally prepared by Russian workers,[2] provided access to several synthetically useful intermediates by extrusion of SO_2 using flash vacuum pyrolysis (FVP) as shown in Scheme 1. Thus, FVP of **1** itself



Scheme 1

gave a good yield of *cis*-divinylsuccinic anhydride **2** and a variety of other tricyclic sulfones **3**, readily obtained from **1**, similarly gave stable *cis*-divinyl compounds **4** which could also be obtained from **2**.[3] The acyclic divinyl intermediates obtained from FVP of bicyclic derivatives **5**, in contrast, underwent spontaneous Cope rearrangement to afford a convenient and stereospecific synthesis of the (*E*,*Z*)-1,5-dienes **6**.[4] More recently we reported the pyrolysis behaviour of Diels–Alder adducts of the isomeric 2,3-dihydrothiophene 1,1-dioxide **7**, and observed both cycloreversion and extrusion of SO_2 and ethene, the latter process making **7** a synthetic equivalent of acetylene for the Diels–Alder reaction.[5] In this paper we describe the preparation of the new [2 + 2] cycloadduct **8** formed between **7** and maleic anhydride, its conversion into various derivatives isomeric with **3** and **5**, and the behaviour of these compounds upon FVP.

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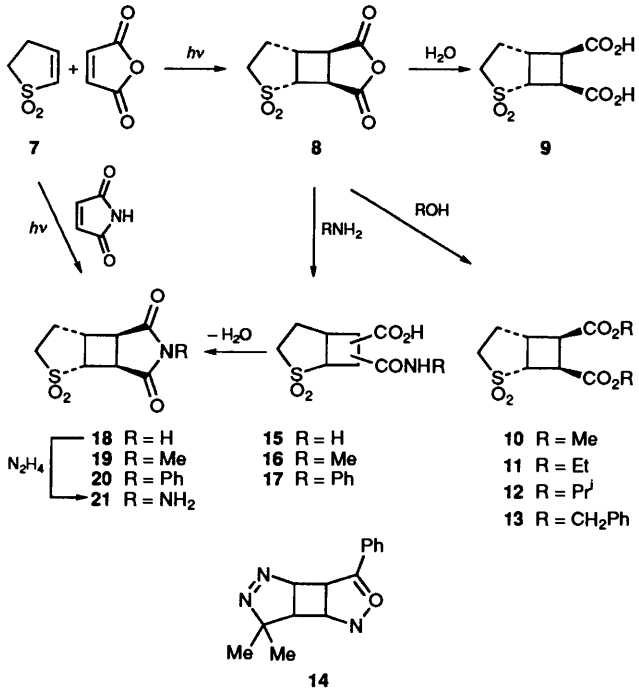
Results and Discussion

Following the procedure for the isomeric anhydride **1**,[2] irradiation of an acetone solution of 2-sulfolene **7** and maleic anhydride afforded the tricyclic anhydride **8** in moderate yield. This was readily converted into the diacid **9** in hot water and to diesters **10–13** by acid catalysed reaction with the appropriate alcohol. The poor solubility of **8** in $CDCl_3$ prevented any



detailed analysis of the ^1H NMR coupling patterns but the more soluble diesters gave good spectra showing the expected slight non-equivalence of the signals owing to the ester groups. The signals due to the bicyclic ring system were complex with all eight protons being distinct and some coupling to four others giving 16 line signals. A selective decoupling study on the 360 MHz ^1H spectrum of dibenzyl ester **13** allowed unambiguous assignment of all the signals and determination of all but one of the coupling constants. Using the numbering scheme shown in Fig. 1 the following coupling constants were determined (in Hz

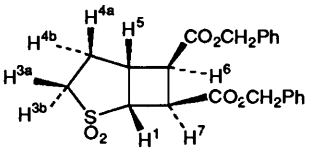
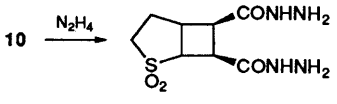


Fig. 1

to nearest whole number): $J_{1,5}$ 8, $J_{1,6}$ 1, $J_{1,7}$ 5, $J_{3a,4a}$ 15, $J_{3a,4b}$ 4, $J_{3b,4a}$ 11, $J_{3b,4b}$ 14, $J_{4a,4b}$ 6, $J_{4a,5}$ 12, $J_{4b,5}$ 2, $J_{5,6}$ 6, $J_{5,7}$ 1 and $J_{6,7}$ 10. Owing to coincidence of the signals $J_{3a,3b}$ could not be determined. It is evident that the *cis* cyclobutane coupling constants of 8 and 10 Hz are considerably larger than the *trans* values of 5 and 6 Hz which supports the *anti* configuration for **13** and thus for **8**. In a similar system **14**[6] the *anti* isomer gave *cis* coupling constants of 5.6 and 7.0 Hz and *trans* values of 2.5 and 2.3 Hz, while the *syn* isomer gave values of 7.0, 8.1, 6.1 and 7.3 Hz. It therefore appears that the [2 + 2] cycloaddition has taken place to give the *anti* product **8** and this is consistent with the isomeric compound **1** whose *anti* stereochemistry has been established by means of an X-ray structure determination.[4]

The 3-sulfolene–maleic anhydride adduct **1** has previously been reported[2,3] to react with primary amines to form the diacid monoamides which could be converted into the corresponding cyclic imides by dehydration. The 2-sulfolene adduct **8** reacted similarly with ammonia, methylamine and aniline to afford diacid monoamides **15**–**17** as mixtures of regioisomers. These were conveniently converted into the corresponding imides **18**–**20** simply by vacuum sublimation. These compounds were highly polar and high melting, the *N*-phenylimide **20**, for example, having a melting point of over 320 °C. The *N*-unsubstituted imine **18** could also be obtained in low yield by direct photochemical reaction between maleimide and 2-sulfolene **7**, while the corresponding reaction with *N*-substituted maleimides resulted only in maleimide dimerisation. This pattern of reactivity has also been observed for the reaction of 3-sulfolene with maleimides.[2] Reaction of the unsubstituted imide **18** with 1 equiv. of hydrazine hydrate gave the *N*-aminoimide **21**. The five-membered ring *N*-amino structure of this compound, as opposed to the alternative six-membered ring hydrazide, is supported by its ready deamination with aqueous nitrous acid to regenerate **18**. Reaction of dimethyl ester **10** with 2.5 equiv. of hydrazine hydrate afforded the dihydrazide **22**,



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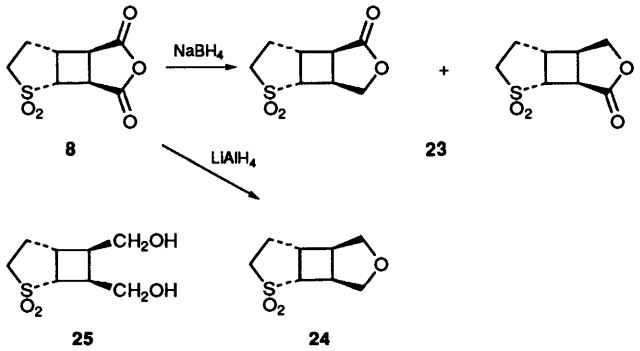
a reaction again consistent with the behaviour of the isomeric compounds based on **1**.[2]

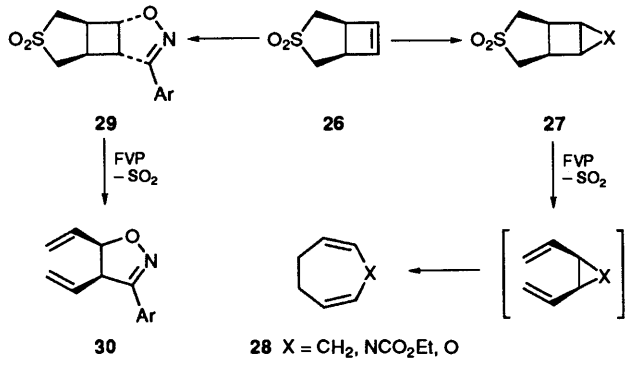
Reduction of anhydride **8** with sodium borohydride in dimethylformamide (DMF) afforded the lactone **23** which was



25 **24**

shown by ^{13}C NMR spectroscopy to exist as a 1:1 mixture of the two possible regioisomers. The corresponding reaction of **1** to give a single symmetrical lactone has already been reported.[3] The two isomeric systems showed a remarkable difference in their reactivity with lithium aluminium hydride. Treatment of either **1**[2] or the derived dimethyl ester[3] with this reagent was previously reported to give the corresponding diol in reasonable yield. In contrast, **8** reacted with $LiAlH_4$ to give the cyclic ether **24** in low yield and dimethyl ester **10** failed to react with excess of the reagent even under forcing conditions [10 h in boiling tetrahydrofuran (THF)] and was recovered unchanged. The reason for this behaviour is unclear but it prevented access to the synthetically useful diol **25**.

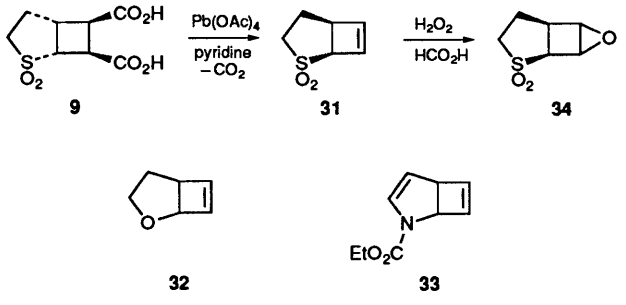
One of the most useful intermediates examined in our previous work was 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide **26**, readily formed by oxidative bis-decarboxylation of the diacid from hydrolysis of **1**.[7] As shown in Scheme 2, the double



29 **26** **27** **30** **28** X = CH_2, NCO_2Et, O

Scheme 2

bond could be functionalised by epoxidation, aziridination and cyclopropanation to give **27** and FVP of these products gave seven-membered ring products **28** by spontaneous Cope rearrangement of the initially formed *cis* divinyl compounds. On the other hand 1,3-dipolar cycloaddition gave products such as **29** which upon FVP gave access to stable divinyl isoxazolines **30**. It was therefore of interest to prepare the isomeric alkene **31** from oxidative bis-decarboxylation of diacid **9**. Unfortunately



9 **31** **34** **32** **33**

this reaction, using lead tetraacetate in pyridine, proceeded in consistently poor yield, but the target compound was obtained and fully characterised. As for the other compounds described here, the aliphatic region of its ^1H NMR spectrum was complex but a selective decoupling study on the 360 MHz spectrum allowed assignment of all the signals and determination of all the coupling constants. Using the numbering scheme shown in Fig. 2 the following values were found (in Hz to nearest whole number): $J_{1,3a}$ 2, $J_{1,5}$ 4, $J_{1,6}$ 1, $J_{3a,3b}$ 14, $J_{3a,4a}$ 7, $J_{3a,4b}$ 1, $J_{3b,4a}$ 14, $J_{3b,4b}$ 7, $J_{4a,4b}$ 14, $J_{4a,5}$ 7, $J_{4b,5}$ 1, $J_{5,7}$ 1, $J_{6,7}$ 3. The observation of 1 Hz coupling diagonally across the four-membered ring, with near zero coupling between 1- and 7-H

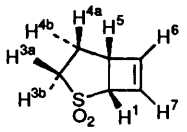
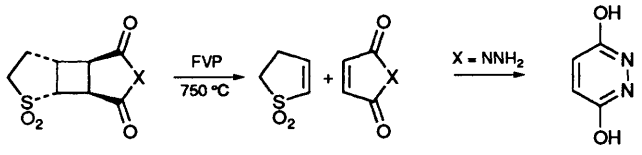


Fig. 2

and between 5- and 6-H is in good agreement with a study by Paquette and co-workers[8] who reported a similar pattern for compounds **32** and **33**. Epoxidation of **31** using performic acid afforded the tricyclic epoxide **34** albeit in low yield.

We previously reported that FVP of a variety of bi- and tricyclic sulfones derived from Diels–Alder cycloaddition of 2-sulfolene **7** resulted either in cycloreversion or in extrusion of ethene and SO_2 depending on the degree of ring strain present.[5] It was envisaged that the [2 + 2] adducts described here might behave similarly, and that the latter process might allow access to cyclobutene anhydride **35** and its derivatives. This compound was recently reported to be a useful acetylene equivalent in Diels–Alder reactions,[9] but the normal route for its preparation involves the rather hazardous low temperature photolysis of an acetone solution containing a high proportion of dissolved acetylene. In the event all the compounds examined were more thermally stable than the isomeric analogues derived from **1** and all the tricyclic examples underwent exclusive [2 + 2] cycloreversion at temperatures in the range 750–800 °C (Scheme 3).



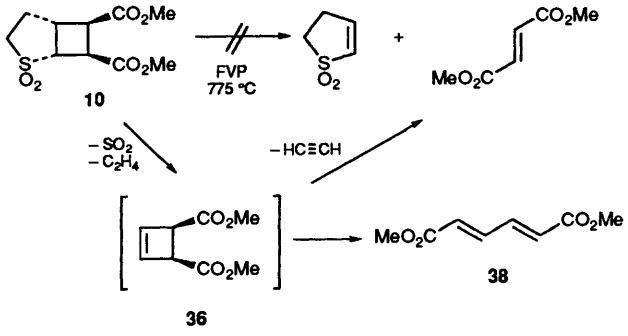
8 X = O
18 X = NH
19 X = NMe
20 X = NPh
21 X = NNH_2

Scheme 3

Thus, **8** gave 2-sulfolene and maleic anhydride and the imides **18–21** similarly gave 2-sulfolene and the maleimides. The cycloreversion of *N*-amino imide **21** was accompanied by isomerisation of the *N*-aminomaleimide to the more stable 3,6-dihydroxypyridazine isomer. As has already been noted, vacuum sublimation of the diacid monoamides **15–17** led to dehydration to the corresponding cyclic imides, so it is not surprising that attempted FVP of these compounds proceeded with dehydration to give the same mixtures of 2-sulfolene and maleimides obtained from the imides **18–20**. Quantitative cycloreversion was also observed for the isomeric mixture of lactones **23** at 750 °C to give 2-sulfolene and butenolide (2,5-dihydrofuran-2-one). Pyrolysis of the cyclic ether **24** was only complete at temperatures of 800 °C and above to give a complex mixture whose components could not be identified, but did not include any of the expected products.

Pyrolysis of the diacid **9** at 750 °C gave mainly 2-sulfolene and maleic anhydride, clearly resulting from dehydration to the anhydride which then fragmented, but there was a small proportion (6%) of benzene. At 850 °C the yields of 2-sulfolene and maleic anhydride were reduced to 20%, there was more benzene (14%), and crotonaldehyde appeared as a significant product (18%). At present we have no good explanation for the formation of this most unexpected product.

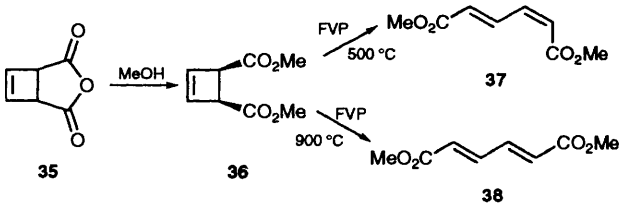
The pyrolysis of the diesters **11** and **12** also gave disappointing results with 2-sulfolene and maleic anhydride as the only identifiable products formed in low yield, presumably by elimination of ethene and propene from the alkyl groups to form **9** which then cyclised to **8** and gave the observed products.



10
36
38

Scheme 4

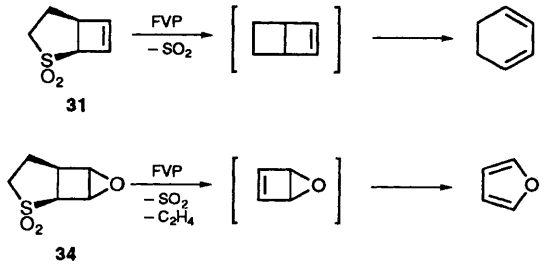
With the dimethyl ester **10** more interesting results were obtained. FVP at 775 °C again gave several unidentified products, but preparative TLC allowed isolation of dimethyl fumarate and (*E*,*E*)-dimethyl hexa-2,4-dienedioate (dimethyl muconate) **38** in low yields. Significantly, no 2-sulfolene was formed in this case, and the isomeric esters dimethyl maleate and (*E*,*Z*)- or (*Z*,*Z*)-dimethyl muconate were also absent. The course of this reaction is most probably as shown in Scheme 4, where initial loss of ethene and SO_2 gives the cyclobutene diester **36**. This can undergo either the well known[10] electrocyclic ring opening to the (*E*,*Z*)-diester **37** followed by thermal isomerisation to the more stable isomer **38** or loss of acetylene to give dimethyl maleate which likewise isomerises to the fumarate. The absence of 2-sulfolene, which was known from the other pyrolyses to be stable under these conditions, rules out the alternative of cycloreversion as a route to the maleate/fumarate. In order to obtain authentic samples of **37** and **38**, the proposed intermediate **36** was prepared by



35
36
37
38

methanolysis of cyclobutene anhydride **35** and subjected to FVP. At 500 °C clean conversion into the (*E*,*Z*)-isomer **37** was observed, while at 900 °C there was complete conversion into the (*E*,*E*)-isomer **38**. In view of the mechanism proposed for the breakdown of **10**, it is surprising that no trace of dimethyl fumarate was formed in the latter reaction. The formation of **36** in a vibrationally excited state by extrusion of ethane and SO_2 perhaps promotes the extrusion of acetylene to give the fumarate, a process which does not occur in the direct pyrolysis of **36**.

The pyrolysis of bicyclic alkene **31** proceeded under much milder conditions than for any of the compounds above. Even at 450 °C there was complete extrusion of SO_2 to form a moderate yield of cyclohexa-1,3-diene accompanied by a little benzene resulting from its dehydrogenation. As shown in Scheme 5, this



31
34

Scheme 5

probably results from electrocyclic ring opening of the bicyclo[2.2.0]hexene formed by loss of SO_2. This type of electrocyclic ring opening is also known for many carbocyclic and heterocyclic compounds with the bicyclo[3.2.0]hept-6-ene ring structure leading to seven-membered ring dienes,[11] but all attempts to induce conversion of **31** into the isomeric 2,3-dihydrothiepine 1,1-dioxide were unsuccessful. The compound was recovered unchanged after prolonged heating in solution at over 200 °C, even in the presence of silver perchlorate or palladium on charcoal. Finally the epoxide **34** was pyrolysed at 550 °C to give furan as the main product, presumably formed as shown in Scheme 5, by extrusion of ethene and SO_2 to give the Dewar isomer of furan which immediately reverts to the normal isomer under the conditions used. It is interesting to note that this result demonstrates the ability of sulfone **31** to act as an equivalent of cyclobutadiene by reaction of the double bond and subsequent pyrolysis.

In conclusion, we have found that the pyrolytic behaviour of the compounds derived from the 2-sulfolene–maleic anhydride adduct **8** is much less useful than that of the isomeric systems derived from **1**. Cycloreversion is the dominant process in most cases and any other products are formed only in low yield. The pyrolysis behaviour of **31** and **34** is perhaps more promising, but an improved method for preparation of **31** is required if it is to be of any value as a synthetic intermediate.

Experimental

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. Infrared spectra were recorded for Nujol mulls on a Perkin-Elmer 157G spectrometer. NMR spectra were recorded for ^1H at 100 MHz on a Varian HA100 instrument or at 360 MHz on a Bruker WH360 instrument and for ^{13}C at 20 MHz on a Varian CFT 20 or at 90 MHz on a Bruker WH360 instrument. Spectra were obtained for solutions in $CDCl_3$ unless otherwise indicated with Me_4Si as internal standard. Coupling constants J are given in Hz. Mass spectra were obtained on a AEI MS902 instrument with electron impact at 70 eV. GC–MS was performed with a Pye 104 chromatograph coupled to a VG Micromass 12 spectrometer. Photochemical reactions were carried out using a 400 W Applied Photophysics medium-pressure mercury lamp in a quartz immersion-well reactor.

Preparation of 9-Oxa-3-thiatricyclo[5.3.0.0^{2,6}]*decane-8,10-dione 3,3-Dioxide* **8**.—A solution of 2,3-dihydrothiophene 1,1-dioxide[12] (2-sulfolene) **7** (10.0 g, 85 mmol) and maleic anhydride (10.0 g, 102 mmol) in acetone (250 cm^3) was irradiated at 400 W for 40 h. The resulting white solid was filtered off and washed well with ether. The filtrate was set aside for several days to allow partial evaporation when further crops were obtained to give *9-oxa-3-thiatricyclo*[5.3.0.0^{2,6}]*decane-8,10-dione, 3,3-dioxide* **8** (6.6 g, 36%) as colourless crystals, m.p. 258–260 °C (Found: C, 44.2; H, 3.65. $C_8H_8O_5S$ requires C, 44.4; H, 3.7%); ν_{max}/cm^{-1} 1862, 1790, 1315, 1307, 1175, 1145, 1125, 1068, 996, 921, 903, 857, 718 and 669; $\delta_H(CD_3SOCD_3)$ 3.9 (1 H, m), 3.6–3.3 (5 H, m) and 2.3–2.0 (2 H, m); m/z 216 (M$^+$, 4%), 172 (5), 152 (4), 108 (51), 95 (10), 80 (93) and 79 (10).

Preparation of 2-Thiabicyclo[3.2.0]*heptane-6,7-dicarboxylic Acid 2,2-Dioxide* **9**.—A mixture of **8** (4.5 g, 21 mmol) and water (40 cm^3) was heated under reflux for 2 h. The clear solution was cooled to 0 °C and the resulting crystals filtered off, washed with ether and vacuum dried to give *2-thiabicyclo*[3.2.0]*heptane-6,7-dicarboxylic acid 2,2-dioxide* **9** (4.2 g, 86%) as colourless cystals, m.p. 198–200 °C (Found: C, 41.1; H, 4.3. $C_8H_{10}O_6S$ requires C, 41.0; H, 4.3%); ν_{max}/cm^{-1} 1722, 1708, 1410, 1293, 1265, 1241, 1228, 1188, 1120, 1090 and 850; $\delta_H(CD_3SOCD_3)$ 11.25 (2 H, br s), 3.7–3.2 (6 H, m) and 2.2–2.0 (2 H, m); m/z 235 (M + 1$^+$, 0.2%), 234 (0.03), 217 (0.9), 216 (1.8), 170 (6), 152 (14), 108 (49), 80 (90) and 79 (100).

Preparation of Dimethyl 2-Thiabicyclo[3.2.0]*heptane-6,7-dicarboxylate 2,2-Dioxide* **10**.—A mixture of **8** (1.0 g, 4.6 mmol) and AR methanol (15 cm^3) containing sulfuric acid (0.05 cm^3) was heated under reflux for 2 h. The product crystallised out on cooling and was filtered off to give *dimethyl 2-thiabicyclo*[3.2.0]*heptane-6,7-dicarboxylate 2,2-dioxide* **10** (0.92 g, 75%) as colourless needles, m.p. 154–155 °C (Found: C, 45.7; H, 5.3. $C_{10}H_{14}O_6S$ requires C, 45.8; H, 5.4%); ν_{max}/cm^{-1} 1746, 1732, 1324, 1301, 1253, 1232, 1148, 1126, 1098, 1075, 1015, 949, 848, 835 and 728; δ_H(360 MHz) 3.82 (1 H, dd, 1-H), 3.73 (1 H, ddd, 7-H), 3.71 (3 H, s, 7-CO_2CH_3), 3.68 (3 H, s, 6-CO_2CH_3), 3.60 (1 H, m, 5-H), 3.27 (1 H, dd, 6-H), 3.16 (2 H, dd, 3-H_2), 2.38 (1 H, m, 4-H) and 2.08 (1 H, m, 4-H); m/z 262 (M$^+$, 0.2%), 231 (54), 198 (45), 171 (12), 166 (77), 139 (58), 138 (35) and 79 (100).

Preparation of Diethyl 2-Thiabicyclo[3.2.0]*heptane-6,7-dicarboxylate 2,2-Dioxide* **11**.—A mixture of **8** (0.50 g, 2.3 mmol) and ethanol (10 cm^3) containing sulfuric acid (0.05 cm^3) was heated under reflux for 2 h. On cooling the product crystallised out and was filtered off, washed with ether and dried to give *diethyl 2-thiabicyclo*[3.2.0]*heptane-6,7-dicarboxylate 2,2-dioxide* **11** (0.55 g, 82%) as colourless needles, m.p. 126–128 °C (Found: C, 49.5; H, 6.05. $C_{12}H_{18}O_6S$ requires C, 49.6; H, 6.2%); ν_{max}/cm^{-1} 1738, 1305, 1270, 1250, 1231, 1124, 1096, 1072, 1019, 916, 858, 753, 725 and 690; δ_H 4.17 (2 H, q, J 7), 4.15 (2 H, q, J 7), 3.85–3.5 (3 H, m), 3.4–3.1 (3 H, m), 2.6–2.0 (2 H, m), 1.27 (3 H, t, J 7) and 1.26 (3 H, t, J 7); m/z 290 (M$^+$, 4%), 245 (100), 226 (15), 217 (30), 180, (65), 171 (18), 153 (51) and 79 (95).

Preparation of Diisopropyl 2-Thiabicyclo[3.2.0]*heptane-6,7-dicarboxylate 2,2-Dioxide* **12**.—A mixture of **8** (0.50 g, 2.3 mmol) and isopropyl alcohol (10 cm^3) containing sulfuric acid (0.05 cm^3) was heated under reflux for 4 h. The solution was evaporated and the colourless oil subjected to chromatography (alumina, Et_2O). This gave a crystalline solid, which was recrystallised from diisopropyl ether to give *diisopropyl 2-thiabicyclo*[3.2.0]*heptane-6,7-dicarboxylate 2,2-dioxide* **12** (0.27 g, 37%) as colourless needles, m.p. 86–87 °C (Found: C, 52.9; H, 7.05. $C_{14}H_{22}O_6S$ requires C, 52.8; H, 7.0%); ν_{max}/cm^{-1} 1738, 1725, 1300, 1270, 1242, 1213, 1180, 1148, 1112, 1048, 901 and 719; δ_H 5.017 (1 H, septet, J 6), 5.011 (1 H, septet, J 6), 3.9–3.5 (3 H, m), 3.3–3.1 (3 H, m), 2.6–1.9 (2 H, m), 1.253 (6 H, d, J 6) and 1.247 (6 H, d, J 6); m/z 318 (M$^+$, 0.5%), 277 (83), 259 (57), 235 (59), 217 (100), 168 (39), 152 (35) and 126 (81).

Preparation of Dibenzyl 2-Thiabicyclo[3.2.0]*heptane-6,7-dicarboxylate 2,2-Dioxide* **13**.—A mixture of **8** (1.0 g, 4.6 mmol) and benzyl alcohol (10 cm^3) containing sulfuric acid (0.05 cm^3) was heated under reflux for 2.5 h. Ether (50 cm^3) was added and the resulting precipitate filtered off, washed with ether and dried to give *dibenzyl 2-thiabicyclo*[3.2.0]*heptane-6,7-dicarboxylate 2,2-dioxide* **13** (0.81 g, 42%) as colourless needles, m.p. 123–125 °C (Found: C, 63.5; H, 5.2. $C_{22}H_{22}O_6S$ requires C, 63.8; H, 5.4%); ν_{max}/cm^{-1} 1740, 1500, 1302, 1273, 1217, 1198, 1178, 1138, 1122, 1095, 1060, 1020, 932, 744 and 696; δ_H(360 MHz) 7.36–7.24 (10 H, m), 5.04 and 4.94 (2 H, AB pattern, J 12), 5.00 and 4.90 (2 H, AB pattern, J 12), 3.85 (1 H, dd, 1-H), 3.79 (1 H, ddd, 7-H), 3.65 (1 H, m, 5-H), 3.30 (1 H, dd, 6-H), 3.18–3.12 (2 H, m, 3-H_2), 2.44–2.33 (1 H, m, 4-H) and 2.11–2.05 (1 H, m, 4-H); m/z 414 (M$^+$, 1.2%), 323 (6), 217 (27), 197 (34), 180 (57), 123 (27), 108 (96), 107 (98), 92 (97) and 91 (100).

Preparation of the 2-Thiabicyclo[3.2.0]*heptane-6,7-dicarboxylic Acid Monoamide 2,2-Dioxides* **15**.—A mixture of **8** (5.0 g,

23.1 mmol) and aqueous ammonia (*d* 0.88; 25 cm^3) was stirred for 12 h. Evaporation gave a white solid (5.49 g). This was purified by precipitation by ether from aqueous methanol to give a mixture of isomers of 2-*thiabicyclo*[3.2.0]*heptane*-6,7-*dicarboxylic acid monoamide* 2,2-*dioxide* **15** (2.5 g, 46%) as colourless crystals, m.p. 198–200 °C (Found: M^+, 233.0363. $C_8H_{11}NO_5S$ requires M^+, 233.0358); ν_{max}/cm^{-1} 3570, 3420, 3160, 1680, 1558, 1292, 1263, 1138, 1126, 1098, 910 and 767; δ_H 8.85 (0.3 H, br s), 6.85 (0.7 H, br s), 5.90 (2 H, br s), 3.5–3.0 (6 H, m) and 2.1–1.9 (2 H, m); *m/z* 233 (M^+, 0.2%), 215 ($M^+ - H_2O$, 30), 172 (6), 151 (8), 136 (7), 123 (35) and 108 (100).

Preparation of the 2-*Thiabicyclo*[3.2.0]*heptane*-6,7-*dicarboxylic Acid Monomethylamide* 2,2-*Dioxides* **16**.—Aqueous methylamine solution (25%, 2.7 cm^3, 22 mmol) was added to a suspension of **8** (1.0 g, 4.6 mmol) in AR methanol (15 cm^3). After being stirred for 24 h the solution was evaporated to give a white solid which was dried to give 2-*thiabicyclo*[3.2.0]*heptane*-6,7-*dicarboxylic acid monomethylamide* 2,2-*dioxide* **16** (0.93 g, 81%) as a mixture of isomers, m.p. 95–105 °C (Found: M^+, 247.0508. $C_9H_{13}NO_5S$ requires M^+, 247.0514); ν_{max}/cm^{-1} 1650, 1564, 1295, 1262, 1116, 970, 907, 770 and 721; δ_H 8.16 (1 H, br s), 5.97 (1 H, br s), 3.6–2.9 (6 H, m), 2.58 and 2.54 (3 H, s for each isomer) and 1.2–0.9 (2 H, m); *m/z* 247 (M^+, 0.3%), 229 ($M^+ - H_2O$, 100), 172 (5), 165 (19), 150 (8), 137 (23) and 108 (100).

Preparation of the 2-*Thiabicyclo*[3.2.0]*heptane*-6,7-*dicarboxylic acid Monoanilide* 2,2-*Dioxides* **17**.—This was based on the literature method for the 3-thia isomer.[2] Aniline (0.44 g, 4.7 mmol) was added to a suspension of **8** (1.0 g, 4.6 mmol) in AR methanol (15 cm^3) and the mixture was stirred for 3 h. Partial evaporation gave a white solid which was filtered off and washed with methanol. Recrystallisation from methanol gave a mixture of the two isomers of 2-*thiabicyclo*[3.2.0]*heptane*-6,7-*dicarboxylic acid monoanilide* 2,2-*dioxide* **17** (1.06 g, 74%) as colourless crystals which decomposed with loss of water at 250–300 °C to the imine which then melted at 322–324 °C. The ^1H NMR showed a 3:2 ratio of the 7-anilide to the 6-anilide: $\delta_H(CD_3SOCD_3$–$CDCl_3)$ 9.79 (0.6 H, s), 9.56 (0.4 H, s), 7.65–7.5 (2 H, m), 7.4–7.0 (3 H, m), 4.0–3.5 (3 H, m), 3.4–3.15 (3 H, m) and 2.5–2.0 (2 H, m) (acid OH not apparent).

In a repeat preparation the solution was not evaporated down after 3 h but the solid filtered off to give the pure 7-anilide isomer: 7-*phenylcarbamoyl*-2-*thiabicyclo*[3.2.0]*heptane*-6-*carboxylic acid* 2,2-*dioxide* (0.78 g, 54%) as colourless crystals, m.p. as above (Found: M^+, 309.0678. $C_{14}H_{15}NO_5S$ requires M^+, 309.0671); ν_{max}/cm^{-1} 3450 (OH), 3330 (NH), 1740, 1674, 1598, 1538, 1499, 1290, 1035, 761, 721 and 708; $\delta_H(CD_3SOCD_3/CDCl_3)$ 12.4 (1 H, br s, OH), 10.18 (1 H, s, NH), 7.6–7.0 (5 H, m), 3.8–3.2 (6 H, m) and 2.3–1.95 (2 H, m); *m/z* 309 (M^+, 2%), 291 (100), 119 (22), 108 (16), 93 (21), 80 (34) and 79 (45).

On storage of the filtrate for 2 days the other isomer crystallised out to give colourless needles (0.52 g, 36%) consisting of the 7-anilide isomer (15%) and 85% of the 6-anilide: 6-*phenylcarbamoyl*-2-*thiabicyclo*[3.2.0]*heptane*-7-*carboxylic acid* 2,2-*dioxide*; ν_{max}/cm^{-1} 3240, 1732, 1679, 1606, 1446, 1298, 1158, 1118, 920, 745 and 690.

Preparation of 3-*Thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]*decane*-8,10-*dione* 3,3-*Dioxide* **18**.—The first method used was based on the literature method for the 4-thia isomer.[2] A solution of maleimide (0.82 g, 8.5 mmol), 2,3-dihydrothiophene 1,1-dioxide **7** (3.0 g, 25.4 mmol) and acetophenone (0.4 cm^3) in acetone (10 cm^3) was irradiated at 400 W for 40 h. The resulting solid was filtered off and washed well with ether. Hot methanol (25 cm^3) was added to the solid and the insoluble maleimide dimer filtered off. When cooled the filtrate gave 3-*thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]*decane*-8-10-*dione* 3,3-*dioxide* **18** (0.31 g, 16%) as colourless crystals, m.p. 255–256 °C (Found: C, 44.85; H, 4.2; N, 6.7. $C_8H_9NO_4S$ requires C, 44.6; H, 4.2; N, 6.5%); ν_{max}/cm^{-1} 3160, 3080, 1780, 1690, 1360, 1312, 1250, 1202, 1181, 1160, 1141, 1096, 910, 826 and 720; $\delta_H(CD_3SOCD_3)$ 11.25 (1 H, s), 3.7–3.1 (6 H, m) and 2.3–2.1 (2 H, m, 5-H_2); *m/z* 215 (M^+, 33%) 123 (24), 108 (48), 80 (48) and 79 (100).

The compound could be obtained more easily and in better yield by subliming the diacid monoamide **15** with loss of water. Thus, when the product from treatment of **8** (1.0 g, 4.6 mmol) with an excess of aqueous ammonia and evaporation was sublimed at 220–250 °C/10^{-2} mmHg, it gave 3-*thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]*decane*-8,10-*dione* 3,3-*dioxide* **18** (0.60 g, 56%) as colourless crystals, m.p. 255–256 °C.

Preparation of 9-*Methyl*-3-*thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]-*decane*-8,10-*dione* 3,3-*Dioxide* **19**.—A sample of monomethylamide **16** (mixture of isomers, 0.50 g) was heated at 130 °C/5 × 10^{-3} mmHg for 2 h. The solid melted, gas was evolved, and finally the product resolidified. Sublimation at 170 °C/5 × 10^{-3} mmHg followed by recrystallisation from AR methanol gave 9-*methyl*-3-*thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]*decane*-8,10-*dione* 3,3-*dioxide* **19** (0.20 g, 43%) as colourless needles, m.p. 190–192 °C (Found: C, 47.4; H, 4.9; N, 6.1. $C_9H_{11}NO_4S$ requires C, 47.2; H, 4.8; N, 6.1%); ν_{max}/cm^{-1} 1780, 1690, 1312, 1301, 1290, 1254, 1134, 1096, 961, 915, 725 and 665; $\delta_H(CD_3SOCD_3)$ 3.7–3.2 (6 H, m), 2.86 (3 H, s) and 2.3–2.1 (2 H, m); *m/z* 229 (M^+, 25%), 165 (8), 137 (15), 108 (22), 80 (58) and 79 (100).

Preparation of 9-*Phenyl*-3-*thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]*decane*-8,10-*dione* 3,3-*Dioxide* **20**.—A sample of monoanilide **17** (mixture of isomers, 0.30 g) was heated at 320 °C/5 × 10^{-3} mmHg. This led to loss of water and sublimation of the product to give 9-*phenyl*-3-*thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]*decane*-8,10-*dione* 3,3-*dioxide* **20** (0.22 g, 81%) as colourless crystals, m.p. 322–325 °C (Found: C, 57.5 H, 4.45; N, 4.75. $C_{14}H_{13}NO_4S$ requires C, 57.7; H, 4.5; N, 4.8%); ν_{max}/cm^{-1} 1861, 1788, 1704, 1492, 1310, 1297, 1165, 1138, 1098, 920, 767, 745 and 697; $\delta_H(CD_3SOCD_3)$ 7.6–7.2 (5 H, m), 3.8–3.2 (6 H, m) and 2.4–2.2 (2 H, m); *m/z* 291 (M^+, 47%), 198 (3), 173 (3), 119 (10), 108 (29), 80 (56) and 79 (100).

Preparation of 9-*Amino*-3-*thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]*decane*-8,10-*dione* 3,3-*Dioxide* **21**.—A solution of **18** (200 mg, 0.93 mmol) and hydrazine hydrate (47 mg, 0.94 mmol) in methanol (5 cm^3) was heated under reflux for 12 h. The solid was filtered off and sublimed at 220–250 °C/10^{-2} mmHg to give 9-*amino*-3-*thia*-9-*azatricyclo*[5.3.0.$0^{2,6}$]*decane*-8,10-*dione* 3,3-*dioxide* **21** (90 mg, 42%) as colourless crystals, m.p. 255–228 °C (Found: C, 41.8; H, 4.4; N, 12.2. $C_8H_{10}N_2O_4S$ requires C, 41.7; H, 4.4; N, 12.2%); ν_{max}/cm^{-1} 3342, 3280, 1787, 1700, 1610, 1304, 1220, 1131, 1103, 920, 727 and 670; $\delta_H(CD_3SOCD_3)$ 5.01 (2 H, s, NH), 3.65–3.2 (6 H, m) and 2.3–2.1 (2 H, m); *m/z* 230 (M^+, 100%), 171 (6), 137 (12), 135 (11), 112 (98), 107 (22) and 79 (38).

Preparation of 2-*Thiabicyclo*[3.2.0]*heptane*-6,7-*dicarbohydrazide* 2,2-*Dioxide* **22**.—This was again based on the literature method for the 3-thia isomer.[2] A solution of **10** (0.50 g, 1.9 mmol) and hydrazine hydrate (0.21 g, 4.2 mmol) in AR methanol (10 cm^3) was heated under reflux for 2 h. The resulting precipitate was filtered off, washed with methanol and dried. Recrystallisation from aqueous methanol–ether gave 2-*thiabicyclo*[3.2.0]*heptane*-6,7-*dicarbohydrazide* 2,2-*dioxide* **22** (0.26 g, 52%) as colourless flakes, m.p. 194–195 °C (Found: 36.7; H, 5.4; N, 21.25. $C_8H_{14}N_4O_4S$ requires C, 36.6; H, 5.4; N, 21.4%);

ν_{max}/cm^{-1} 3380, 3345, 3310, 3165 (NH), 1743, 1731, 1680, 1663, 1596, 1297, 1268, 1138, 1093, 1028, 961 and 725; δ_H(CD_3SOCD_3) 8.93 (1 H, br s, 7-NH), 8.78 (1 H, br s, 6-NH), 4.17 (4 H, br s, NH_2), 3.7–3.1 (6 H, m) and 2.2–1.9 (2 H, m); *m/z* 262 (M^+, 0.03%), 230 (82), 171 (7), 137 (17), 135 (13), 112 (100), 107 (26) and 97 (15).

Preparation of 9-*Oxa*-3-*thiatricyclo*[5.3.0.0^{2,6}]*decane*-8- *and* -10-*one* 3,3-*Dioxide* **23**.—A solution of **8** (2.0 g, 9.26 mmol) in dry dimethylformamide (8 cm^3) was stirred at 0 °C while a solution of sodium borohydride (0.40 g, 10.6 mmol) in dry dimethylformamide (5 cm^3) was added over 5 min. After being stirred for 2 h at room temperature the solution was cooled in ice and hydrochloric acid (6 mol dm^{-3}; 4 cm^3) was carefully added. The mixture was extracted with methylene chloride (3 × 20 cm^3) and the combined extracts were then washed with water (6 × 50 ml), dried and evaporated to give a white solid. Recrystallisation of this from ethyl acetate gave an isomeric mixture of 9-*oxa*-3-*thiatricyclo*[5.3.0.0^{2,6}]*decane*-8- and -10-*one* 3,3-*dioxide* **23** (0.35 g, 19%) as colourless crystals, m.p. 155–170 °C (Found: C, 47.5; H, 5.0. $C_8H_{10}O_4S$ requires C, 47.5; H, 5.0%); ν_{max}/cm^{-1} 1760, 1305, 1276, 1180, 1140, 1118, 997, 951, 779, 702, 676 and 655; δ_H($CDCl_3$–CD_3SOCD_3, 4:1) 4.48 (2 H, m), 3.7–3.0 (6 H, m) and 2.4–2.1 (2 H, m); δ_C(CD_3SOCD_3) 178.2, 176.4, 73.4, 71.9, 57.5, 56.3, 47.0, 46.4, 41.6, 39.7 (2 C), 38.2, 36.3, 35.0, 26.2 and 25.7; *m/z* 202 (M^+, 29%), 184 (1), 153 (1), 119 (4), 107 (5), 93 (18) and 79 (100).

Preparation of 3-*Oxa*-9-*thiatricyclo*[5.3.0.0^{2,6}]*decane* 3,3-*Dioxide* **24**.—Compound 8 (10.0 g, 46 mmol) was added slowly to a stirred suspension of lithium aluminium hydride (2.0 g, 53 mmol) in dry tetrahydrofuran (100 cm^3) under nitrogen. After the mixture had been heated under reflux for 8 h the excess of lithium aluminium hydride was destroyed by successive addition of water (2 cm^3) in tetrahydrofuran (10 cm^3), 15% aqueous sodium hydroxide (2 cm^3) and finally water (2 cm^3). The inorganic solids were filtered off and washed with acetone (250 cm^3). The filtrate was evaporated and the residue kugelrohr distilled at 200–220 °C/0.4 mmHg to give a colourless oil which crystallised with time. Recrystallisation from ethanol gave 3-*oxa*-9-*thiatricyclo*[5.3.0.0^{2,6}]*decane* 3,3-*dioxide* **24** (0.50 g, 6%) as colourless needles, m.p. 129–131 °C (Found: C, 50.9; H, 6.4. $C_8H_{12}O_3S$ requires C, 51.0; H, 6.4%); ν_{max}/cm^{-1} 1294, 1273, 1124, 1097, 1068, 1025, 917, 908, 889, 840, 768, 701 and 690; δ_H 4.0 (2 H, m), 3.6–3.4 (2 H, m), 3.3–3.0 (4 H, m), 2.9–2.6 (2 H, m) and 2.5–1.9 (2 H, m); *m/z* 188 (M^+, 22%), 134 (18, 129 (21), 119 (12), 95 (37), 94 (70), 81 (40) and 79 (100).

Preparation of 2-*Thiabicyclo*[3.2.0]*hept*-6-*ene* 2,2-*Dioxide* **31**.—The diacid **9** (5.0 g, 21.4 mmol) was dissolved in dry pyridine (50 cm^3) and oxygen was bubbled through the solution for 15 min. Dry lead tetraacetate (14.2 g, 32 mmol) was then added in one portion and the mixture heated to 70 °C. Vigorous gas evolution took place to give finally a clear dark brown solution. After being stirred for 10 min at 70–80 °C this was poured into nitric acid (1.5 mol dm^{-3}; 800 cm^3). Extraction with CH_2Cl_2 followed by drying and evaporation gave a yellow oil. Preparative TLC of this on alumina (Et_2O–hexane, 4:1) gave 2-*thiabicyclo*[3.2.0]*hept*-6-*ene* 2,2-*dioxide* **31** (0.16 g, 5%) as colourless oil, n_D^{25} 1.5105 (Found: M^+, 144.0242. $C_6H_8O_2S$ requires M^+, 144.0245); ν_{max}/cm^{-1} 1415, 1303, 1270, 1225, 1125, 1105, 924, 867, 799 and 688; δ_H(360 MHz) 6.33 and 6.22 (2 H, AB pattern, *J* 2, 6, 7-H), 3.49 (1 H, dd, *J* 4, 2, 1-H), 3.74 (1 H, dd, *J* 7, 4, 5-H), 3.49 (1 H, dt, *J* 14, 14, 7, 3b-H), 2.92 (1 H, ddd, *J* 14, 7, 2, 3a-H), 2.23 (1 H, 7 lines, *J* 14, 14, 7, 7, 4a-H) and 2.06 (1 H, dd, *J* 14, 7, 4b-H); δ_C(90 MHz) 143.1 (C-7), 134.0 (C-6), 60.9 (C-1), 46.1 (C-5), 44.5 (C-3) and 21.9 (C-4); *m/z* 144 (M^+, 12%), 119 (5), 95 (31), 88 (14), 79 (100) and 77 (31).

Preparation of 8-*Oxa*-3-*thiatricyclo*[5.1.0.0^{2,6}]*octane* 3,3-*Dioxide* **34**.—A solution of **31** (50 mg 0.35 mmol) and 30% hydrogen peroxide (1.0 cm^3, 9 mmol) in formic acid (5 cm^3) was stirred at 60 °C for 50 h. Evaporation gave a colourless oil (70 mg) which on preparative TLC (alumina, Et_2O) followed by recrystallisation from diisopropyl ether–hexane (1:1) gave 8-*oxa*-3-*thiatricyclo*[5.1.0.0^{2,6}]*octane* 3,3-*dioxide* **34** (16 mg, 30%) as colourless crystals, m.p. 135–136 °C (Found: C, 45.2; H, 4.9. $C_6H_8O_3S$ requires C, 45.0; H, 5.0%); ν_{max}($CHCl_3$)/cm^{-1} 1320, 1185, 1140, 1130, 1102 and 978; δ_H(360 MHz) 4.23 (1 H, m), 3.93 (1 H, m), 3.44 (1 H, m), 3.28 (1 H, t of d, *J* 14, 7), 3.19 (1 H, m), 3.09 (1 H, m), 2.43 (1 H, 7 lines, *J* 14, 14, 7, 7) and 2.26 (1 H, m); *m/z* (M^+ not apparent), 119 (7%), 95 (9), 84 (15), 81 (17), 79 (13) and 68 (100, furan).

Flash Vacuum Pyrolysis.—The general techniques and apparatus have been described previously.[9] The products from small-scale pyrolyses were dissolved in $CDCl_3$ and analysed directly by ^{1}H NMR and/or GLC, while the products from larger, preparative-scale pyrolyses were isolated, purified and characterised in the normal way. Yields for small-scale pyrolyses were determined by adding an accurately weighed quantity of a solvent such as CH_2Cl_2 to the NMR solution and comparing integrals in the ^{1}H spectrum, a procedure estimated to be accurate to ± 10%. The pyrolysis conditions are given as follows: (weight of compound pyrolysed, furnace temperature, mean pressure during pyrolysis, inlet temperature).

FVP of anhydride **8**. Pyrolysis at temperatures below 700 °C led mainly to recovery of unchanged starting material. FVP of **8** (67 mg, 750 °C, 10^{-3} mmHg, inlet 160–180 °C) gave a small quantity of starting material at the furnace exit (10 mg) but the bulk of the product was shown by ^{1}H NMR to be 2,3-dihydrothiophene 1,1-dioxide and maleic anhydride.

FVP of **8** (80 mg, 800 °C) gave unchanged starting material (5 mg), insoluble polymer (2 mg) and mainly 2,3-dihydrothiophene 1,1-dioxide and maleic anhydride, in yields of 69 and 62% respectively, based on the reacted starting material.

FVP of diacid **9**. FVP of **9** (53 mg, 750 °C, 5 × 10^{-3} mmHg, inlet 170–190 °C) gave a yellow oil whose ^{1}H NMR showed it to consist of 2,3-dihydrothiophene 1,1-dioxide, maleic anhydride, a small proportion of benzene and other minor components in the δ_H 7.5–5.5 range. The presence of 2,3-dihydrothiophene 1,1-dioxide was confirmed by TLC (alumina, Et_2O) and of benzene by GC (10% PEGA, 55 °C). Calibration of the NMR gave the yields as: 2,3-dihydrothiophene 1,1-dioxide (62%), maleic anhydride (77%) and benzene (6%).

FVP of **9** (57 mg, 850 °C, 3 × 10^{-3} mmHg, inlet 170–200 °C) gave less 2,3-dihydrothiophene 1,1-dioxide and maleic anhydride, more benzene and several new products of which crotonaldehyde was the most abundant. The product was identical with authentic crotonaldehyde on GC and ^{1}H NMR and was conclusively identified by GC–MS. Calibration of the NMR gave the yields as: 2,3-dihydrothiophene 1,1-dioxide (22%), maleic anhydride (18%), benzene (14%) and crotonaldehyde (18%, assuming one molecule produced per molecule diacid). These four products accounted for 75% of the protons in the condensed product.

FVP of dimethyl ester **10**. FVP of **10** (250 mg, 775 °C, 10^{-3} mmHg, inlet 120–150 °C) gave a white oily solid whose ^{1}H NMR showed a complex pattern with several methyl signals at δ_H 3.8 and a forest of peaks in the δ_H 7.4–5.4 region. The only products which were identified by comparison with authentic samples on GC (2% NPGS, 150 °C) were dimethyl fumarate and (*E*,*E*)-dimethyl hexa-2,4-dienedioate ('dimethyl muconate'). The corresponding *Z*-isomers were not present. Preparative TLC on alumina (Et_2O) gave colourless crystals (15 mg) which proved to be a 1:1 mixture of dimethyl fumarate

(5% yield) and (*E,E*)-dimethyl muconate (5%) (^{1}H NMR, TLC).

Preparation of authentic dimethyl muconates. 3-Oxabicyclo[3.2.0]hept-6-ene-2,4-dione **35** was heated under reflux in methanol with a trace of sulfuric acid to give *cis*-dimethyl cyclobutene-3,4-dicarboxylate **36** in 70% yield after distillation.

FVP of **36** (75 mg, 500 °C, 10^{-2} mmHg, inlet 25 °C) gave pure (*E,Z*)-dimethyl muconate **37** (54 mg, 74%) as colourless crystals, m.p. 74–75 °C (lit.,[13] 75 °C).

FVP of **36** (72 mg, 900 °C, 10^{-2} mmHg, inlet 25 °C) gave pure (*E,E*)-dimethyl muconate **38** (49 mg, 68%) as colourless crystals, m.p. 145–150 °C (lit.,[13] 156–157 °C).

FVP of diethyl ester **10**. FVP of **10** (40 mg, 750 °C, 2×10^{-3} mmHg, inlet 110–130 °C) gave a brown oil whose ^{1}H NMR showed the presence of 2,3-dihydrothiophene 1,1-dioxide (1.9 mg, 12%) and maleic anhydride (0.5 mg, 4%) as well as many other components with peaks in the δ_H 7.5–5.5 region. The ethyl groups had been almost entirely lost and there was a broad OH signal at δ_H 7.9. Apart from 2,3-dihydrothiophene 1,1-dioxide there were no other TLC mobile components and no other component could be identified. Pyrolysis at 800 °C gave complete loss of ethyl groups with the other products unchanged.

FVP of diisopropyl ester **11**. FVP of **11** (45 mg, 700 °C, 2×10^{-3} mmHg, inlet 120–150 °C) gave products almost identical with those obtained from the diethyl ester above. There were low yields of 2,3-dihydrothiophene 1,1-dioxide and maleic anhydride, very little isopropyl group left and an identical pattern between δ_H 7.5 and 5.5 caused by-products which could not be identified.

FVP of imide **18**. FVP of **18** (60 mg, 675 °C, 5×10^{-3} mmHg, inlet 220–230 °C) gave largely the unchanged starting material (52 mg) but also volatile products which proved to be a 1:1 mixture of maleimide and 2,3-dihydrothiophene 1,1-dioxide (^{1}H NMR, TLC).

FVP of **18** (48 mg, 750 °C, 5×10^{-3} mmHg, inlet 220–230 °C) gave only 5 mg starting material and a high yield of the retro-[2 + 2] products. Calibration of the NMR gave the yields as: maleimide (82%) and 2,3-dihydrothiophene 1,1-dioxide (75%).

FVP of N*-methylimide* **19**. FVP of **19** (62 mg, 750 °C, 5×10^{-3} mmHg, inlet 180–200 °C) gave 2 mg of starting material and a 1:1 mixture of *N*-methylmaleimide and 2,3-dihydrothiophene 1,1-dioxide (^{1}H NMR, TLC). Calibration of the NMR gave the yields as 60 and 64% respectively.

Pyrolysis at 700 °C gave a similar result but with 10% unchanged starting material.

FVP of N*-phenylimide* **20**. FVP of **20** (46 mg, 750 °C, 3×10^{-3} mmHg, inlet 280–300 °C) gave a small quantity (5 mg) of unchanged starting material but the bulk of the product consisted of a 1:1 mixture of *N*-phenylmaleimide and 2,3-dihydrothiophene 1,1-dioxide (^{1}H NMR, TLC).

FVP of N*-aminoimide* **21**. FVP of **21** (39 mg, 750 °C, 5×10^{-3} mmHg, inlet 180–200 °C) gave 2,3-dihydrothiophene 1,1-dioxide in the colder part of the trap (^{1}H NMR, TLC) and 3,6-dihydroxypyridazine near the furnace exit; IR and ^{1}H NMR [$\delta_H(CD_3SOCD_3)$ 11.33 (1 H, br s) and 6.98 (2 H, s)] in good agreement with literature spectra.[14]

FVP of lactones **23**. FVP of **23** (isomeric mixture, 36 mg, 750 °C, 5×10^{-3} mmHg, inlet 140–160 °C) gave complete reaction to a 1:1 mixture of 2,3-dihydrothiophene 1,1-dioxide (^{1}H NMR, TLC) and 2,5-dihydrofuran-2-one ('butenolide') (^{1}H NMR identical with authentic sample prepared by the method of Takano *et al.*[15]).

FVP of cyclic ether **24**. Pyrolysis at 750 °C gave mainly the unchanged starting material. FVP of **24** (35 mg, 800 °C, 3×10^{-3}, inlet 100–130 °C) gave little starting material (2 mg), a small quantity of polymer (1 mg) and a colourless oil. NMR of this showed many peaks in the regions δ_H 7.5–4.5 and 3.5–1.5. None of these could be identified. GC (2% NPGS, 200 °C) showed a single component which was proved by GC–MS to be a trace of the starting material. 2,3-Dihydrothiophene 1,1-dioxide and 2,5-dihydrofuran were not present, nor was 3-oxabicyclo[3.2.0]hept-6-ene or its ring-expanded isomer 2,7-dihydrooxepine.

FVP of the cyclobutene **31**. Pyrolysis at 350 °C gave no reaction. FVP of **31** (17 mg, 450 °C, 5×10^{-3} mmHg, inlet 30–80 °C) gave a yellow oil whose NMR showed the main component to be cyclohexa-1,3-diene with a small proportion of benzene. GC (10% PEGA, 55 °C) confirmed the presence of these two products and calibration of the NMR gave the yields as 30 and 5% respectively.

Attempted solution pyrolysis of the cyclobutene **31**. A solution of **31** in deuteriochloroform showed no change after being heated in a sealed NMR tube in boiling toluene for 120 h and in boiling hexachlorobutadiene (b.p. 210–220 °C) for 120 h. Addition of silver perchlorate and heating at 210–220 °C for a further 36 h gave no change. A solution of the sulfone in hexachlorobutadiene also remained unchanged after prolonged heating at 210–220 °C, even on addition of silver perchlorate or 10% palladium on charcoal.

FVP of epoxide **34**. FVP of **34** (8.5 mg, 550 °C, 2×10^{-3} mmHg, inlet 120–140 °C) gave a colourless liquid whose GC (10% PEGA, 55 °C) showed it to contain furan. The NMR (360 MHz) confirmed this and also showed a large proportion of the unchanged starting material. The yield of furan was estimated to be about 10%.

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