

## Effect of Ring Strain on the Formation and Pyrolysis of some Diels–Alder Adducts of 2-Sulfolene (2,3-Dihydrothiophene 1,1-Dioxide) and Maleic Anhydride with 1,3-Dienes and Products Derived Therefrom

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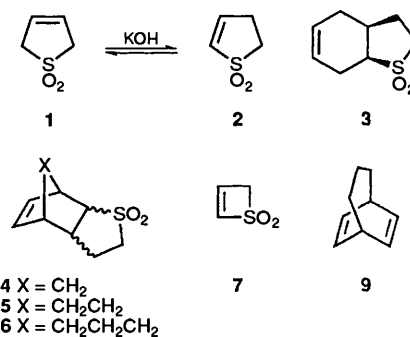
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7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide **3** and the 2,5-bridged analogues **4–6** formed by Diels–Alder reaction of 2,3-dihydrothiophene 1,1-dioxide (2-sulfolene) **2** with butadiene and cyclic 1,3-dienes are found, upon flash vacuum pyrolysis, either to lose SO<sub>2</sub> and ethene, or to undergo a retro-Diels–Alder reaction, depending on the degree of ring strain present. The epoxides **10**, **13** and **17** of these compounds decompose exclusively by loss of SO<sub>2</sub> and ethene to give the mono-epoxides of cyclic 1,4-dienes which undergo further reactions under the pyrolysis conditions. The same final products can also be obtained by extrusion of CO and CO<sub>2</sub> from the epoxides **12**, **16** and **19** of the corresponding diene–maleic anhydride adducts. In the case of the furan–maleic anhydride adduct, its epoxide **20** fragments by a retro-Diels–Alder reaction to give 1,4-dioxine, which, at high temperatures, is transformed into acrylaldehyde. Pyrolysis of the aziridines **22–24**, formed by photochemical reaction of the diene–maleic anhydride adducts with ethyl azidoformate, generally gives complex decomposition products, although for the methylene-bridged compound **22** there is good evidence for the generation of a 1,4-dihydropyridine *via* a retro-Diels–Alder reaction.

Although 2,5-dihydrothiophene 1,1-dioxide (3-sulfolene) **1** enjoys considerable synthetic popularity as a masked form of butadiene,<sup>1</sup> it exhibits very weak dienophilic behaviour;<sup>2</sup> prolonged heating with butadiene or cyclopentadiene, either in the presence or absence of a Lewis acid catalyst, results only in self-condensation of the dienes. In contrast, Alder reported as early as 1938<sup>3</sup> that the isomeric 2,3-dihydrothiophene 1,1-dioxide (2-sulfolene) **2** undergoes cycloadditions with both butadiene and cyclopentadiene to form 7-thiabicyclo[4.3.0]non-3-ene 7,7-dioxide **3** and the bridged sulfone **4**, respectively. Despite these early preparations, the chemistry of such adducts has been neglected and their pyrolytic behaviour is unknown although, in principle, elimination of SO<sub>2</sub> (and ethene) offers access to compounds formally derived from cycloaddition of the 1,3-diene to acetylene, which itself is practically unreactive except under drastic conditions.<sup>4</sup> In view of the sustained interest,<sup>5</sup> including our own,<sup>6</sup> in the development of reliable acetylene Diels–Alder synthons, we have exploited the dienophilicity of **2** towards 1,3-dienes and prepared a range of cycloadducts with varying ring strain. The paper describes the results of their thermal fragmentation under flash vacuum pyrolytic (FVP) conditions, as well as that of compounds derived from the adducts by epoxidation of their double bonds. For comparison purposes, the pyrolysis of the corresponding maleic anhydride adducts is also reported. Hydrolysis and oxidative decarboxylation of the latter is one of the most successful methods developed<sup>7</sup> as a substitute for the use of acetylene, but direct extrusion of CO<sub>2</sub> and CO by flash pyrolysis remains a possible, but relatively unexplored procedure for the formation of the required double bond.

### Results and Discussion

Access to 2-sulfolene **2** can be gained readily by stirring its commercially available 3-isomer **1** in aqueous potassium hydroxide at room temperature (see Scheme 1).<sup>8</sup> Formation of



Scheme 1

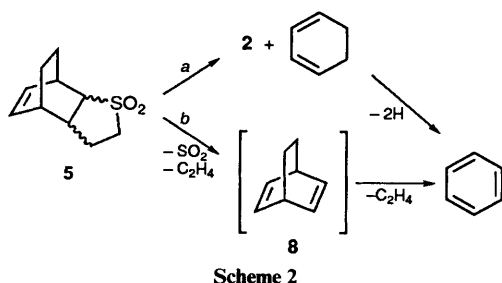
the cycloadducts **3–6** was accomplished by heating a benzene solution of **2** with butadiene, cyclopentadiene, cyclohexa-1,3-diene and cyclohepta-1,3-diene, respectively, in an autoclave at 150–200 °C for 20–110 h. Unfortunately, the reactivity of **2** proved not to be very high and the yields ranged from 36% for **4** to only 4% in the case of **6**. No reaction occurred with furan. As originally observed by Alder,<sup>3</sup> the methylene bridged compound **4** was formed as an oily, non-crystallisable solid, presumably because of the presence of a mixture of *exo*- and *endo*-isomers. This was confirmed in the case of **6** by its <sup>13</sup>C NMR spectrum which clearly showed the presence of both isomers in equal amounts. As a rule, there is a pronounced tendency for many conjugated alkenes, *e.g.* maleic anhydride<sup>9</sup> (*vide infra*) to afford almost exclusively the *endo*-isomer, especially with cyclopentadiene, owing to favourable secondary orbital interactions which are absent in the transition state leading to the *exo*-isomer.<sup>10</sup> The lower stereoselectivity shown by **2** parallels that observed for the related thiete dioxide **7**,<sup>11</sup> which, according to MNDO-calculations,<sup>12</sup> gives rise to negligible secondary interactions. In this situation, provided there are no prevailing steric or dipolar repulsions in either the *endo*- or *exo*-transition states, equal amounts of each adduct may be anticipated.

When subjected to FVP, the adducts **3–6** fragmented by

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different pathways depending upon the degree of ring strain. The non-bridged compound **3**, with little if any ring strain, lost  $\text{SO}_2$  and ethene to give cyclohexa-1,4-diene which underwent thermal dehydrogenation to benzene by different amounts depending on the pyrolysis temperature. At  $675^\circ\text{C}$ , conversion of **3** into cyclohexa-1,4-diene and benzene occurred in low yield in the ratio of 2:5, whereas raising the temperature to  $750^\circ\text{C}$  resulted in complete reaction and the overwhelming formation of benzene (82%) with only small amounts of cyclohexa-1,4-diene (8%). Conversion of the latter into benzene is a previously recognised pyrolytic process<sup>13</sup> and arises from a concerted symmetry-allowed 1,4-elimination of hydrogen.

An entirely different process was observed for the adduct **4**. At temperatures above  $650^\circ\text{C}$ , breakdown proceeded by a retro-Diels-Alder reaction to give a high yield of 2-sulfolene and cyclopentadiene, a process clearly favoured by the release of ring strain due to the introduction of a methylene bridge. Cycloreversion also occurred with the ethylene-bridged adduct **5** (path a, Scheme 2) but, in this case, the process competed with

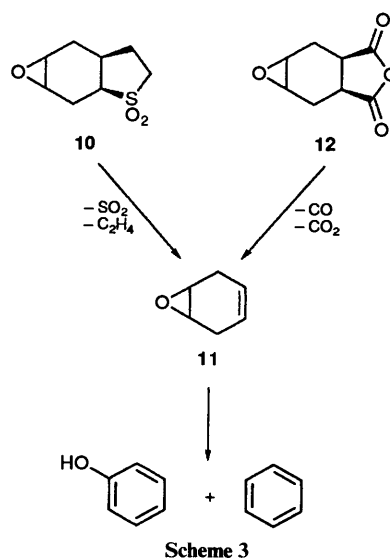


thermal fragmentation by loss of  $\text{SO}_2$  and ethene (path *b*). No bicyclo[2.2.2]octa-2,5-diene **8** could be detected in the pyrolysate which in the temperature range of  $650\text{--}750^\circ\text{C}$  consisted of only cyclohexa-1,3-diene, 2-sulfolene and benzene. This is not surprising since **8** is known<sup>14</sup> to lose ethene readily when heated to give benzene. Control experiments showed that cyclohexa-1,3-diene is also converted into benzene in increasing amounts as the pyrolysis temperature is raised. When this complicating factor is taken into account, together with the concomitant decomposition of 2-sulfolene to  $\text{SO}_2$ , ethene and acetylene, an analysis of the product ratios established that path *b* (loss of  $\text{SO}_2$  and ethene) accounted for *ca.* 70% of the total reaction at  $750^\circ\text{C}$ .

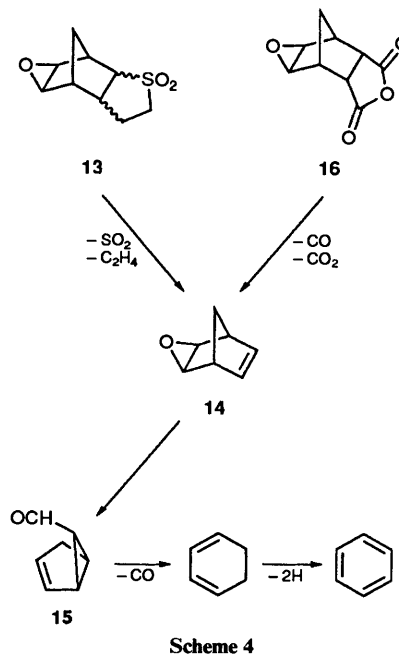
With its flexible three-carbon bridge, the sulfone **6** is even less strained, and from the foregoing pattern of reactivity, might be expected to fragment exclusively by loss of  $\text{SO}_2$  and ethene to yield bicyclo[3.2.2]nona-6,8-diene **9**. In fact, pyrolysis of **6** did produce a major product with *m/z* 120 corresponding to **9**, but it was more resistant to thermal decomposition and no breakdown occurred until  $800^\circ\text{C}$ . As a result, the pyrolysate also contained decomposition products and low yields of toluene and ethylbenzene which presumably arose by cleavage of the carbon bridge under the more severe pyrolysis conditions.

Conceptually, elaboration of the double bond in cycloadducts **4** and **5** should arrest thermal cleavage by cycloreversion since it removes much of the driving force for diene formation. With this in mind, we prepared the epoxides **13** and **17** by oxidation of the corresponding alkenes and compared their thermal breakdown with that of the epoxide **10** from the non-bridged alkene **3** which resisted cycloreversion.

As expected, pyrolysis of the epoxides resulted in each case in extrusion of  $\text{SO}_2$  and ethene to give diene monoepoxides which, in turn, underwent further thermal reactions. Thus, at  $750^\circ\text{C}$ , **10** gave a mixture of benzene and phenol in yields of 72 and 5% respectively, presumably *via* the intermediate cyclohexa-1,4-diene monoepoxide **11** (Scheme 3). The inter-

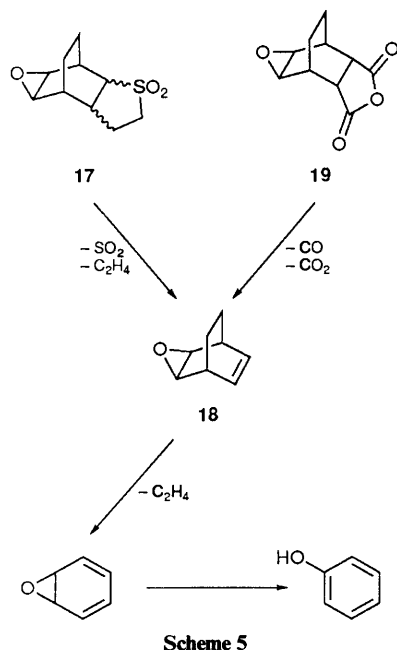


mediacy of **11** is supported by the observation that pyrolysis of an authentic sample, prepared by oxidation of cyclohexa-1,4-diene, under the same conditions also gave benzene and phenol, albeit in 39 and 10% yield, respectively. Pyrolysis of the epoxide **13** at  $750^\circ\text{C}$  produced benzene as the sole identifiable product in 33% yield. The proposed mechanism for its formation is outlined in Scheme 4 and involves the initial extrusion of  $\text{SO}_2$



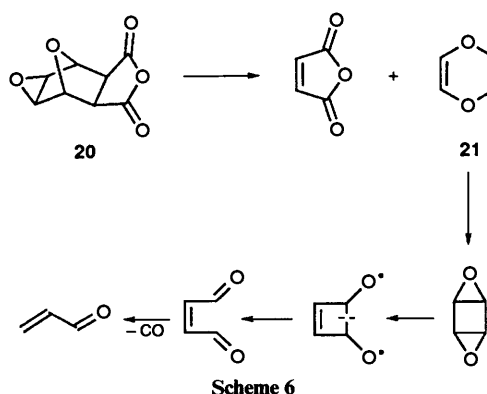
and ethene to give the monoepoxide **14** of bicyclo[2.2.1]hept-2-ene. This compound is known<sup>15,16</sup> to be thermally unstable and undergoes a facile rearrangement to the bicyclic aldehyde **15**, which is transformed into benzene, probably *via* loss of hydrogen from cyclohexa-1,3-diene (*vide supra*). Evidence in support of this pathway was obtained from the independent pyrolyses of the proposed intermediates **14** and **15**. At  $750^\circ\text{C}$ , the former compound gave benzene (42%) and cyclohexa-1,3-diene (5%), whilst under the same conditions, the latter yielded benzene (32%) and cyclohexa-1,3-diene (6%). The mechanism for the conversion of **15** into cyclohexa-1,3-diene is uncertain, but the decarbonylation of aldehydes to give hydrocarbons at temperatures above  $500^\circ\text{C}$  is well established.<sup>17</sup> On pyrolysis

at 750 °C, the epoxide **17** gave phenol in 73% yield. This can be explained by the reaction sequence shown in Scheme 5, whereby



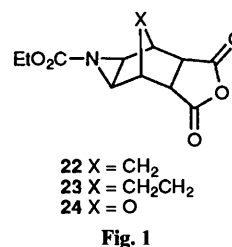
initial loss of SO<sub>2</sub> and ethene affords the monoepoxide of bicyclo[2.2.2]octa-2,5-diene **18**. The latter then loses ethene, in the same way as the parent hydrocarbon **8**, to give benzene epoxide which readily isomerises to phenol.<sup>18</sup>

These pyrolyses demonstrate that 2-sulfolene **2** can function as an acetylene dienophilic equivalent by thermal extrusion of SO<sub>2</sub> and ethene, but only under certain circumstances, otherwise ring strain in the adduct promotes cycloreversion unless this process is arrested by functionalisation of the double bond. Loss of SO<sub>2</sub> and ethene from **2** is akin to the thermal decomposition of maleic anhydride which also generates acetylene by elimination of CO<sub>2</sub> and CO at high temperatures.<sup>19</sup> Attempts to emulate this behaviour in Diels–Alder adducts of maleic anhydride with cyclic 1,3-dienes failed; in every case studied, pyrolysis led to a clean and quantitative cycloreversion, irrespective of the degree of ring strain. However, as observed for the adducts of 2-sulfolene, epoxidation of the double bond induced a beneficial change in their mode of thermal fragmentation. Thus, pyrolysis of the epoxides **12**, **16** and **19** proceeded with loss of CO<sub>2</sub> and CO to give the same products as obtained from the corresponding sulfones by loss of SO<sub>2</sub> and ethene (Schemes 3–5), although in each case an increase in temperature of 50–100 °C was needed for complete reaction. Specifically, the epoxide **12** decomposed at 800 °C to give benzene (30%) and phenol (12%), whilst at 775 °C, **16** produced benzene (41%) and cyclohexa-1,3-diene (11%), and **19** gave a 72% yield of phenol at 850 °C. In these transformations, maleic anhydride serves as a dienophilic acetylene synthon in the same manner observed for 2-sulfolene **2**. The oxygen-bridged epoxy anhydride **20** behaved differently; on pyrolysis at 725 °C, it decomposed by a retro-Diels–Alder reaction to give maleic anhydride (40%) and 1,4-dioxine **21** (15%), together with a 20% yield of acrylaldehyde. The mechanism for formation of the acrylaldehyde is not well understood, but rearrangement with loss of CO from 1,4-dioxine **21** by a secondary process such as that shown in Scheme 6 is required. This is evident from separate pyrolysis experiments in which the proportion of acrylaldehyde was observed to increase with temperature at the expense of **21**, until at 900 °C, the only identifiable products were acrylaldehyde (40%) and benzene (5%), formed by its



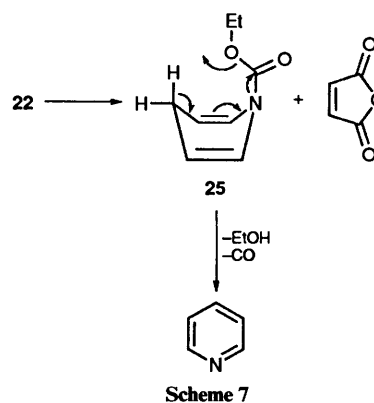
decomposition. This was confirmed by independent pyrolyses of acrylaldehyde which, in addition to benzene, produced aromatic tars.

The pyrolysis of **20** is unusual in that the retro-Diels–Alder reaction still occurs after elaboration of the double bond in the cycloadduct. In an attempt to extend the scope of this little exploited type of reaction,<sup>20</sup> the pyrolysis of the *N*-ethoxy-carbonylaziridines **22–24** (see Fig. 1) was carried out. These



compounds were obtained in moderate yield by photolysis of the respective anhydrides in neat ethyl azidoformate. The same reaction with the butadiene–maleic anhydride adduct gave a product which failed to crystallise and could not be readily purified.

Heating of the methylene-bridged aziridine **22** above its melting point led to extensive decomposition, but on FVP at 725 °C, it gave an orange polymer, together with maleic anhydride and pyridine, both of which were formed in 46% yield. A possible mechanism for this decomposition is shown in Scheme 7 and involves cycloreversion of **22** to give the dihydropyridine **25**



which is transformed into pyridine by concerted loss of CO and ethanol, although radical fragmentation of **25** could also explain the observed products. This is supported by the observation that the product mixture from a pyrolysis at lower temperature (675 °C) consisted of pyridine (10%), ethanol (8%) and a deep red oil (possibly **25**) that, on warming to room temperature, formed the same orange polymer in greater quantity. Significantly,

formation of an orange polymer was observed during a previous preparation of 1,4-dihydropyridine.<sup>21</sup>

Similar pyrolyses of aziridines **23** and **24** at 725 °C also led to the formation of maleic anhydride and ethanol, together with benzene from **23** and furan from **24**, but in each case, extensive decomposition occurred and the products were formed in low yield.

On the basis of these results, it is evident that 2-sulfolene **2**, and to a lesser extent maleic anhydride, offer some scope as acetylene Diels–Alder synthons by pyrolysis in the gas phase, but only after elaboration of the double bond in the cycloadducts. Even under these circumstances, the gain in stabilisation achieved by eliminating maleic anhydride is sufficient for unwanted cycloreversion to become the dominant process for its adducts, e.g. compounds **20** and **22**. The difference in the pyrolytic behaviour for the adducts of maleic anhydride and 2-sulfolene is mirrored in their relative dienophilicities which for the latter is poor and an obvious limitation on its use as an acetylene equivalent. A further drawback is that pyrolytic cleavage of the adducts requires high temperatures which may lead to decomposition of the desired products in secondary processes.

## Experimental

General procedures and instrumentation are as described previously.<sup>6</sup> Preparative GLC was carried out on a Carlo Erba Strumentazione Fractovap 2450 instrument using a 0.85 m × 12 mm column of 30% polyethyleneglycol adipate on Chromosorb A (40–60 mesh). Unless otherwise stated, NMR spectra were obtained at 100 MHz (<sup>1</sup>H) or 25 MHz (<sup>13</sup>C) for solutions in CDCl<sub>3</sub> with Me<sub>4</sub>Si as reference. Coupling constants *J* are given in Hz.

*Preparation of Unsaturated Sulfoxes.*—(a) *cis*-7-Thiabicyclo[4.3.0]non-3-ene 7,7-dioxide **3**. A solution of 2,3-dihydrothiophene 1,1-dioxide **2** (2-sulfolene) (4.0 g, 34 mmol) and buta-1,3-diene (3.2 g, 59 mmol) in dry benzene (40 cm<sup>3</sup>) was heated in an autoclave at 180 °C for 66 h. Evaporation of solvent followed by chromatography of the residue on alumina (Et<sub>2</sub>O as eluent) gave recovered 2-sulfolene **2** (2.68 g) and the desired product. This was recrystallised from ethanol to give the title compound **3** (1.56 g, 27%) as colourless needles, m.p. 93–94 °C (lit.,<sup>3</sup> 94–95 °C) (Found: C, 55.7; H, 6.8. Calc. for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>S: C, 55.8; H, 7.0%;  $\nu_{\max}/\text{cm}^{-1}$  1295, 1228, 1135, 1100, 953, 935, 920, 868, 765 and 659;  $\delta_{\text{H}}$  5.69 (2 H, s), 3.25–3.05 (3 H, m), 2.9–2.5 (1 H, m), 2.45–2.35 (2 H, m) and 2.2–1.85 (4 H, m); *m/z* 172 (M<sup>+</sup>, 1.7%), 107 (15), 106 (85), 105 (10), 91 (25) and 79 (100).

(b) 3-Thiatricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene 3,3-dioxide **4**. A solution of 2-sulfolene **2** (5.0 g, 42 mmol) and freshly prepared cyclopentadiene (3.2 g, 59 mmol) in dry benzene (40 cm<sup>3</sup>) was heated in an autoclave at 150 °C for 20 h. Evaporation followed by chromatography gave recovered 2-sulfolene (1.96 g) and the desired product. Vacuum sublimation of this at 100 °C and 0.2 mmHg gave title compound **4** (2.85 g, 36%) as a colourless non-crystalline solid, m.p. 141–143 °C (lit.,<sup>3</sup> 141–142 °C) (Found: C, 58.55; H, 6.6. Calc. for C<sub>9</sub>H<sub>12</sub>O<sub>2</sub>S: C, 58.7; H, 6.6%;  $\nu_{\max}/\text{cm}^{-1}$  (CHCl<sub>3</sub>) 2978, 1450, 1410, 1347, 1305, 1220, 1172, 1135, 1104, 955, 909, 901 and 811;  $\delta_{\text{H}}$  6.36 (2 H, s), 3.68–3.55 (1 H, m), 3.4–1.8 (7 H, m) and 1.60 and 1.42 (2 H, AB pattern, *J* 8); *m/z* 184 (M<sup>+</sup>, 10%), 119 (18), 118 (26), 105 (8), 92 (7), 91 (17), 79 (12) and 66 (100).

(c) 3-Thiatricyclo[5.2.2.0<sup>2,6</sup>]undec-8-ene 3,3-dioxide **5**. A solution of 2-sulfolene **2** (8.0 g, 68 mmol) and cyclohexa-1,3-diene (5.0 g, 62 mmol) in dry benzene (30 cm<sup>3</sup>) was heated in an autoclave at 190 °C for 110 h. Evaporation followed by chromatography gave recovered **2** (5.5 g) and the desired product. This was recrystallised from ethanol to give the title compound **5** (2.16 g, 18%) as colourless needles, m.p. 88–89 °C

(Found: C, 60.8; H, 7.2. C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>S requires C, 60.5; H, 7.1%);  $\nu_{\max}/\text{cm}^{-1}$  1414, 1305, 1210, 1169, 1120, 956, 927, 890, 844, 720 and 672;  $\delta_{\text{H}}$  6.32 (2 H, m), 3.3–3.16 (2 H, m), 2.4–2.1 (1 H, m), 2.0–1.8 (1 H, m) and 1.58 and 1.35 (4 H, superimposed AB patterns, *J* 10); *m/z* 198 (M<sup>+</sup>, 32%), 134 (14), 119 (25), 105 (41), 92 (49), 91 (68), 80 (96), 79 (50) and 78 (100).

(d) 3-Thiatricyclo[5.3.2.0<sup>2,6</sup>]dodec-11-ene 3,3-dioxide **6**. A solution of 2-sulfolene **2** (5.3 g, 45.2 mmol) and cyclohepta-1,3-diene<sup>22</sup> (4.0 g, 42.6 mmol) in dry benzene (25 cm<sup>3</sup>) was heated in an autoclave at 150 °C for 48 h. Evaporation followed by chromatography gave recovered **2** (4.8 g) and the desired product. After preparative TLC this gave the title compound **6** (0.33 g, 4%) as a colourless oil (Found: M, 212.086. C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>S requires M, 212.087);  $\nu_{\max}/\text{cm}^{-1}$  1500, 1445, 1300, 1127, 1105 and 750;  $\delta_{\text{H}}$  6.45–6.25 and 6.2–6.1 (2 H, *exo* and *endo* isomers), 3.7–2.7 (6 H, m) and 2.4–1.4 (8 H, m);  $\delta_{\text{C}}$  (90 MHz) 136.87, 134.81, 132.85 and 132.05 (C-11, -12, *exo* and *endo*), 65.98 and 64.34 (C-2, *exo* and *endo*), 51.58 (2 C), 51.39 (2 C), 50.16, 47.53, 46.02, 43.08, 41.92, 37.81, 31.18, 28.29 (2 C), 27.05, 23.46 and 22.81; *m/z* 212 (M<sup>+</sup>, 1.4%), 184 (2), 146 (1.2), 133 (1), 118 (15), 105 (16), 91 (62) and 66 (100).

*FVP of Unsaturated Sulfoxes 3–6.*—The general techniques and apparatus have been described previously.<sup>6</sup> The products from small-scale pyrolyses were dissolved in CDCl<sub>3</sub> and analysed directly by <sup>1</sup>H NMR and/or GLC, while the products from larger, preparative-scale pyrolyses were isolated, purified and characterised in the normal way. The pyrolysis conditions are given as follows: mass of compound pyrolysed, furnace temperature, mean pressure during pyrolysis, inlet temperature.

(a) *Compound 3*. Pyrolysis of **3** (78 mg, 675 °C, 2 × 10<sup>-3</sup> mmHg, 40–80 °C) gave unchanged **3** (73 mg) and a yellow liquid which consisted of benzene and cyclohexa-1,4-diene in yields of 43 and 17% respectively, based on reacted **3**. FVP of **3** (80 mg, 750 °C, 3 × 10<sup>-3</sup> mmHg, 40–90 °C) gave a colourless polymer (5 mg) and a liquid which contained benzene (82% yield) and cyclohexa-1,4-diene (8%).

(b) *Compound 4*. Pyrolysis of **4** (54 mg, 750 °C, 2 × 10<sup>-3</sup> mmHg, 40–80 °C) gave a solid and a liquid which were found to be 2-sulfolene (85%) and cyclopentadiene (70%), respectively.

(c) *Compound 5*. Pyrolysis of **5** (42 mg, 675 °C, 4 × 10<sup>-3</sup> mmHg, 40–90 °C) gave polymeric material (3 mg) and a colourless oil containing unchanged **5** (22 mg), benzene (4.6 mg), cyclohexa-1,3-diene (1.8 mg) and 2-sulfolene (5.2 mg). FVP of **5** (53 mg, 750 °C, 2 × 10<sup>-3</sup> mmHg, inlet 40–100 °C) gave polymer (2 mg), benzene (8.9 mg), cyclohexa-1,3-diene (2.0 mg) and 2-sulfolene (5.4 mg).

(d) *Compound 6*. Pyrolysis of **6** (27 mg, 800 °C, 3 × 10<sup>-3</sup> mmHg, 150–200 °C) gave a brown oil. Analysis by GLC–MS showed one major component with *m/z* 120 and several minor components including toluene and ethylbenzene.

*Pyrolysis of Epoxy Sulfoxes.*—The preparation of compounds **10**, **13** and **17** was described in a previous report.<sup>23</sup>

(a) *Compound 10*. Pyrolysis of **10** (25 mg, 750 °C, 10<sup>-3</sup> mmHg, 25–50 °C) gave polymeric material (1 mg) and a colourless liquid which contained benzene and phenol in yields of 72 and 5%, respectively.

(b) *Compound 11*. Pyrolysis of **11**<sup>24</sup> (60 mg, 750 °C, 10<sup>-2</sup> mmHg, 20 °C) gave a polymer (2 mg) and a colourless liquid which contained unchanged **11**, benzene, and phenol in yields of 6, 39 and 10%, respectively.

(c) *Compound 13*. Pyrolysis of **13** (35 mg, 750 °C, 2 × 10<sup>-3</sup> mmHg, 70–120 °C) gave a liquid which contained a 33% yield of benzene and several minor components which were not identified.

(d) *Compound 14*. Pyrolysis of **14**<sup>15</sup> (49 mg, 75 °C, 5 × 10<sup>-3</sup> mmHg, 25–50 °C) gave a colourless liquid containing benzene

(42% yield), cyclohexa-1,3-diene (5%) and several minor components.

(e) **Compound 15**. Pyrolysis of **15**<sup>16</sup> (58 mg, 750 °C,  $2 \times 10^{-2}$  mmHg, 25 °C) gave a yellow liquid containing benzene (32% yield), cyclohexa-1,3-diene (6%), unchanged **15** (6%) and several minor components.

(f) **Compound 17**. Pyrolysis of **17** (28 mg, 750 °C,  $2 \times 10^{-3}$  mmHg, 120–140 °C) gave a colourless solid which was identified as phenol (73% yield).

*Pyrolysis of Epoxy Anhydrides.*—(a) **Compound 12**. Pyrolysis of **12**<sup>25</sup> (40 mg, 800 °C,  $5 \times 10^{-3}$  mmHg, 160–180 °C) gave a colourless solid which consisted of unchanged **12** (2 mg), benzene (30% yield), phenol (12%) and several minor components.

(b) **Compound 16**. Pyrolysis of **16**<sup>26</sup> (30 mg, 775 °C,  $2 \times 10^{-3}$  mmHg, 100–130 °C) gave a colourless liquid which contained benzene (41% yield), cyclohex-1,3-diene (11%) and minor components (5%).

(c) **Compound 19**. Pyrolysis of **19**<sup>27</sup> (31 mg, 850 °C,  $5 \times 10^{-3}$  mmHg, 110–130 °C) gave unchanged **19** (2 mg) and a colourless solid which proved to be phenol (72% yield).

(d) **Compound 20**. Pyrolysis of **20**<sup>28</sup> (1.0 g, 725 °C,  $3 \times 10^{-3}$  mmHg, 140–180 °C) gave unchanged **20** (0.2 g) and a colourless liquid containing maleic anhydride (40% yield), acrylaldehyde and 1,4-dioxine. Preparative GLC (55 °C) yielded acrolein (62 mg, 20%) and 1,4-dioxine (69 mg, 15%);  $\nu_{\max}/\text{cm}^{-1}$  (CDCl<sub>3</sub>) 3125, 1986, 1680, 1642, 1585, 1450, 1280, 1045, 1012 and 988 (good agreement with lit. spectrum); <sup>29</sup>  $\delta_{\text{H}}$  5.55 (4 H, s);  $\delta_{\text{C}}$  127.28 (fully coupled, dd, *J* 197.2 and 16.4); *m/z* 84 (M<sup>+</sup>, 100%), 56 (9), 55 (54), 54 (16), 42 (8) and 40 (8). Pyrolysis of **20** at 900 °C gave acrylaldehyde and benzene in yields of 40 and 5%, respectively.

*Pyrolysis of Aziridines.*—The preparation of compounds **22**, **23** and **24** were described in a previous report.<sup>30</sup>

(a) **Compound 22**. Pyrolysis of **22** (50 mg, 675 °C,  $2 \times 10^{-3}$  mmHg, 140–160 °C) gave a dark red oil which on warming formed an orange polymer (10 mg) and an oil containing maleic anhydride (48% yield), pyridine (10%) and ethanol (8%). Pyrolysis of **22** (52 mg, 725 °C) gave less of the orange polymer and soluble products which were identified as maleic anhydride (46%), and pyridine (46%).

(b) **Compound 23**. Pyrolysis of **23** (39 mg, 725 °C,  $2 \times 10^{-3}$  mmHg, 160–180 °C) gave a yellow oil containing maleic anhydride (20% yield), benzene (18%) and ethanol (48%).

(c) **Compound 24**. Pyrolysis of **24** (23 mg, 725 °C,  $2 \times 10^{-3}$  mmHg, 140–150 °C) gave a yellow oil containing maleic anhydride (20% yield), furan (17%) and ethanol (10%).

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