Macrocyclic Thia-alkenolides Formed by Intramolecular 'Ene' Reactions of Thioaldehydes

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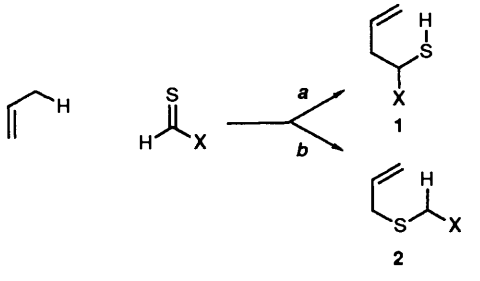
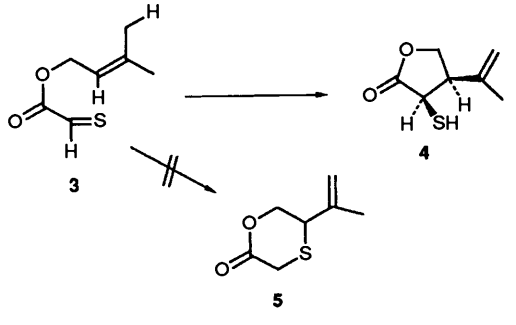
The crystalline acids which are formally cycloadducts of cyclopentadiene and the thioaldehyde thioxoacetic acid [(thioformyl)formic acid] (HO_2C·CHS) have been converted into a series of esters with the alkenols CH_2=CH[CH_2]$_n$OH. These cycloadduct esters, **8** and **9**, when subjected to flash vacuum pyrolysis (FVP) at ~500 °C, liberated the corresponding alkenyl thioxoacetates, **10**, which underwent intramolecular 'ene' reactions to give a series of thia-alkenolides having 6- to 11-membered rings. The 3-thianon-5-en-9-olide **11d** has been transformed, by standard reactions, into 3-vinylhex-2-en-6-olide, **20**, with removal of sulfur. The sulfoxides **28** of the cyclopentadiene adducts have been employed similarly as precursors for the corresponding thioxoacetate ester *S*-oxides (sulfines). Under FVP conditions, intramolecular cyclisation of the allyl **33** and the homoallyl **29** sulfines gave furan-2(5*H*)-one **35** and 5,6-dihydro-2-pyrone, **31**, respectively. The prenyl derivative **37** gave a mixture of the simple product furan-2(5*H*)-one **35** and its 4-isopropenyl derivative **39**. Generally, fumarate esters were formed from sulfines that had failed to cyclise.

In earlier papers[1] we reported that various allylic and homoallylic thioxoacetic [(thioformyl)formic] esters, RO_2C·CHS, liberated as transient intermediates by thermolysis of their anthracene and cyclopentadiene cycloadducts, underwent intramolecular 'ene' reactions. In all cases, the enophilic thioaldehyde group attacked an allylic component of the alkenyl group with C–C bond formation (pathway *a* in Scheme 1) to form a thiol **1**, rather than with C–S bond formation (pathway *b*) to form a sulfide **2**. For example (Scheme 2), the



Scheme 1



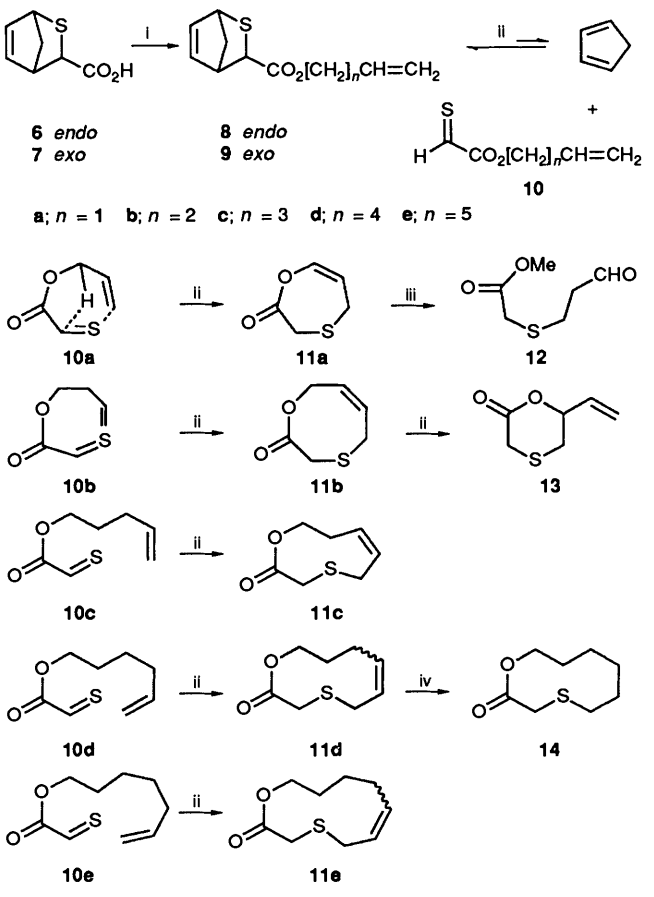
Scheme 2

prenyl ester **3** gave exclusively the α-mercapto-γ-lactone **4** rather than the thia-δ-lactone **5**. As discussed earlier,[1b] the outcome of concerted intramolecular 'ene' reactions of thioaldehydes must depend more on conformational than electronic effects, since thioxoacetate esters under *inter*molecular 'ene' reactions preferentially with C–S bond formation (pathway *b*). The transformations reported previously may be classified[2b] as Type [1, 1], *e.g.* **3** ⟶ **4**, or the less common Type [2, 1] intramolecular 'ene' reactions. The literature[2] contains many examples of both these reaction Types involving other enophilic components. We report here[3] a set of the rarely observed Type [3, 2] reactions, proceeding with the electronically favoured C–S bond formation and the production, in useful preparative yields, of thialactones with 6- to 11-membered rings (Scheme 3).

Synthesis of Thia-alkenolides.—The conditions of flash vacuum pyrolysis[4] (FVP) were ideally suited for this purpose. At low pressure, the productive, unimolecular reactions, *i.e.* dissociation of the cycloadduct precursor (*e.g.*, **8**) and cyclisation of the liberated thioaldehyde **10**, can proceed without competitive, bimolecular recombination of the thioaldehyde with cyclopentadiene or polymerisation of the thioaldehyde. The cyclopentadiene adducts **8** and **9** were employed because they are more volatile than the corresponding anthracene adducts; the dissociation of the cycloadducts is unlikely to be rate limiting at the high temperatures of the pyrolysis tube.† As before,[1] the required esters **8** and **9** were prepared from the corresponding acids[5,7] **6** and **7** and alcohols by condensation with *N,N'*-carbonyldi-imidazole. Generally, mixtures of the esters **8** and **9** (*endo*:*exo* ratio ~7:3) were evaporated slowly at 50–150 °C and ~10^{-4} mbar‡ through a horizontal silica tube maintained at ~500 °C. The products were collected in a trap cooled in liquid nitrogen, then were allowed to warm up to room temperature after addition of dichloromethane to the trap. Evaporation of the dichloromethane and cyclopentadiene gave the products **11** together with lesser amounts of polymeric material believed to arise from the thioaldehydes **10** which had incompletely reacted in the hot tube. Separation of products was readily achieved on account of the low solubility of the polymers in dichloromethane. Variation of the reaction time and temperature was,

† The dissociation rates of cycloadducts of thioxoacetate esters and cyclopentadiene have not been measured. However, the ethyl esters of the *endo* (**6**) and *exo* (**7**) acids gave the same equilibrium mixture (*endo*:*exo* ratio ~3:7), by dissociation and recombination, when heated (111 C) in toluene under reflux for 7 h.[5] The corresponding anthracene adduct **25b** dissociates with a half-life of *ca.* 2 h at 100 °C.[6]

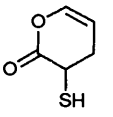
‡ 1 bar = 10^5 Pa.



Scheme 3 *Reagents and conditions:* i, $CH_2{=}CH[CH_2]_nOH$ in THF at 20 °C with carbonyldiimidazole, and ROLi as catalyst; ii, FVP, typically at 500 °C and ~1 × 10^{-4} mbar; iii, SiO_2 in MeOH at 20 °C; iv, $(KO_2C)_2N_2$ and AcOH in aq. MeOH at 20 °C

to some extent, successful in reducing the quantity of polymeric by-products. However, complete optimisation of conditions was not attempted once yields of ~60% of purified thialactones had been achieved.

The thioaldehyde **10a** gave the thiahexenolide **11a** (60%) and some insoluble polymer. None of the alternative, possible product **15** was detected (^{1}H NMR spectroscopy). Therefore, 'ene' cyclisation (see **10a**) had occurred by a Type [3, 2][2b] rather than Type [3, 1][2b] mechanism. The structure **11a** was readily deduced spectroscopically, and confirmation came from the compound's methanolysis, to form the aldehyde **12**, observed when the lactone was chromatographed on silica. The homoallylic esters **8b** and **9b** gave mixtures having compositions dependent upon the pyrolysis temperature. At 600 °C, the thiapentanolide **13** was obtained (34%) along with polymer. At 400 °C, a substantial amount (28%) of the starting materials **8b** and **9b** was recovered together with a new product, the thiaheptenolide **11b** (14%). The presence of only traces of the thiapentanolide **13** was indicated by TLC. Finally, at 500 °C, the reaction mixture contained the esters **8b** and **9b** (11%), the thiaheptenolide **11b** (13%), and the thiapentanolide **13** (29%), together with some polymer. Clearly, an 'ene' reaction, **10b** ⟶ **11b**, and a [3, 3] sigmatropic rearrangement, **11b** ⟶ **13**, had occurred successively in the pyrolysis tube. The starting materials **8b** and **9b** recovered at lower temperatures probably arose, at least in part, from recombination of the thioaldehyde **10b** and cyclopentadiene in the cold trap, once its contents were allowed to warm up. Dissociation* of cycloadducts of type **8** and **9** occurs quite readily in toluene at 111 °C and would be rapid at 400 °C; very likely the 'ene' cyclisation is the rate-limiting process.



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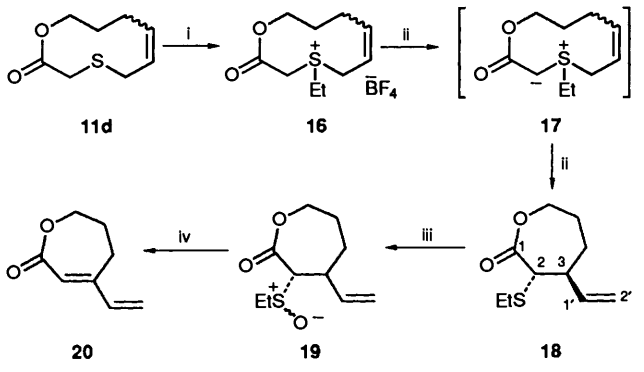
Pyrolysis of the cycloadducts **8c** and **9c** at 500 °C gave, apart from some solid polymer, essentially one product, the oily thiaoctenolide **11c**. The ^{1}H and ^{13}C spectra indicated the formation very largely of a single diastereoisomer, presumably the *Z* cycloalkene **11c**, $J_{5,6}$ 11.0 Hz. However, a very weak set of ^{13}C signals suggested the presence of some *E* isomer. The yield of the nine-membered ring lactone **11c** (57% after purification) was not significantly lower than that of the product **11a** with a seven-membered ring. This observation prompted experiments with higher homologues. Thus, the cycloadducts **8d** and **9d** gave, at 500 °C, the thianonenolides **11d** (63%), as a ~2:1 mixture of geometrical isomers, which could not be separated by chromatography on silica plates. The mixture crystallised from light petroleum, but the well formed crystals, m.p. 34 °C, still had essentially the same composition. The ratio of *Z* and *E* isomers was determined by ^{1}H and ^{13}C NMR spectroscopy. Analysis of the complex ^{1}H spectrum was not straightforward, but a *E* configuration was assigned to the major isomer, which showed a vicinal olefinic coupling constant of 15 Hz. Reduction of the mixture **11d** with diimide, generated from dipotassium azodicarboxylate, was inefficient, but gave a mixture of the dihydro derivative **14** and a small amount of the cycloalkene **11d** (largely the major cycloalkene isomer), separable by TLC on silica plates. It was not clear whether the 'ene' cyclisation had proceeded directly, *i.e.* non-stereospecifically, to give both geometrical isomers **11d** in a 2:1 ratio, or whether *Z*–*E* isomerisation had occurred subsequently at the high pyrolysis temperature. In an attempt to test the latter possibility, the original mixture **11d** was passed again through the pyrolysis tube at 500 °C. However, the mixture was recovered without any significant change in composition. Consequently, no firm conclusion can be reached. The 'ene' cyclisation may have been non-stereospecific; alternatively, thermal isomerism may have proceeded thereafter to give an equilibrium or near-equilibrium mixture. A very similar result was obtained from the 'ene' reaction of the heptenyl ester **10e**, generated as usual at 500 °C from the cycloadducts **8e** and **9e**. The thiadecenolide **11e** was obtained (66%), again as an inseparable, ~2:1 mixture of geometrical isomers. The approximate composition was easily determined from the ^{1}H and ^{13}C NMR spectra, but the former was too complex to permit assignment of configuration to the components. Reduction with diimide gave, inefficiently, the corresponding thiadecanolide.

The foregoing experiments show how ω-vinyl alcohols may be converted, in two preparative steps, into thialactones having 7- to 11-membered rings. There was no noticeable decline in yield with increasing ring size, and consequently the homologous series might well be extended further. Also, similar amides of thioxoacetic acid or α-keto thioaldehydes might give the corresponding thialactams or thiacycloalkenones. Recently, Motoki *et al.* reported[8] the analogous cyclisation of *o*-(alkenyloxy)thiobenzophenones to give benzoxathiocines and benzoxathiecines, having newly formed 8- and 10-membered rings, respectively. Interestingly, corresponding reactions to form 9-, 11-, or 13-membered rings did not take place (*cf.* the thia-alkenolides **11c**, **e**). To our knowledge, these were the first recorded examples of Type III thiocarbonyl 'ene' reactions.

* See footnote † on page 191.

To demonstrate the synthetic potential of the thia-alkenolides **11**, the isomeric thianonenolides **11d** were subjected to a standard series[9] of transformations for ring contraction and removal of sulfur (Scheme 4). Treatment of the 2:1 mixture



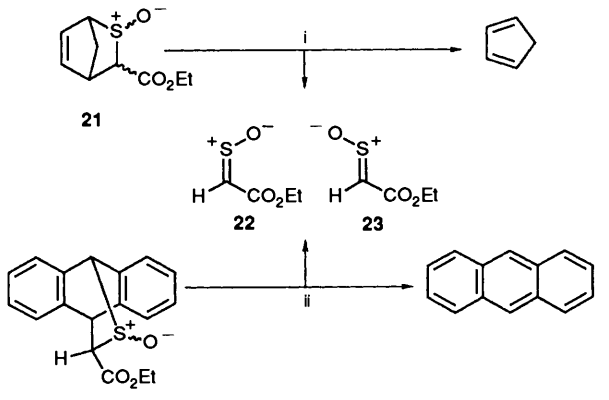
11d **16** **17** **18** **19** **20**

Scheme 4 *Reagents and conditions:* i, $Et_3O^+BF_4^-$ in CH_2Cl_2 at 20 °C; ii, DBN in MeCN at 0 °C; iii, AcOOH in CH_2Cl_2 at 20 °C; iv, heat in PhH or PhMe at 80 or 111 °C, or FVP at 500 °C

of geometrical isomers **11d** successively with triethyloxonium fluoroborate at room temperature and 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) at 0 °C gave, *via* the sulfonium salt **16** and the transient ylide **17**, the hexanolide derivative **18**, in 83% overall yield. This product **18** was judged from its ^1H and ^{13}C NMR spectra to consist very largely of a single stereoisomer, even though it was formed from a mixture of stereoisomeric precursors. Perhaps the DBN had effected epimerisation at C-2 in the lactone, to produce predominantly one isomer, assigned for this reason the *trans* configuration **18**. Weak signals in the ^1H spectrum might have arisen from the *cis* isomer (see Experimental section). The lactone **18** was oxidised at room temperature cleanly with peracetic acid to give a mixture of stereoisomeric sulfoxides **19**. When these were heated under reflux in benzene, partial conversion into the diene **20** was observed. It appeared that the minor sulfoxide epimer had undergone elimination much more rapidly than the major epimer. Almost complete conversion was achieved in refluxing toluene, but complete elimination was most conveniently effected by FVP at 500 °C.

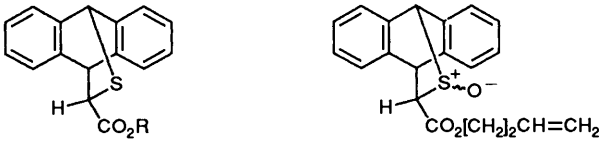
Thioaldehyde S-Oxides (Sulfines).—The ease with which kinetically unfavourable 'ene' reactions had been achieved by FVP encouraged us to investigate the corresponding thioaldehyde *S*-oxides (sulfines). We had found[10] that the sulfoxides **21**, derived from the *endo* and *exo* cycloadducts of cyclopentadiene and ethyl thioxoacetate, underwent retro-Diels–Alder cleavage to give the (*Z*)-**22** or (*E*)-sulfine **23**, depending upon the stereochemistry of the precursor **21** (Scheme 5). The sulfoxides **24**, derived from the corresponding cycloadduct **25b** of anthracene and ethyl thioxoacetate, behaved similarly. Furthermore, cycloadducts of the sulfines were cleaved faster than those of the thioaldehyde. Generally, sulfines undergo cycloadditions with conjugated dienes (the reactions in Scheme 5 are reversible) and 1,3-dipoles,[11] and allyl vinyl sulfoxides rearrange to give homoallylsulfines.[12] However, other pericyclic reactions of sulfines have not apparently been observed.[11] As a prelude to studies on the *S*-oxides of alkenyl thioxoacetates, control experiments were carried out with the ethyl esters **22** and **23**.

When a mixture of the anthracene sulfoxides **24**[10] (*cis*:*trans* ratio ~1:2.5) was subjected to FVP at 500 °C, the major products, apart from anthracene, were sulfur (52%) and diethyl fumarate (64%). In this experiment, as in subsequent pyrolyses, some sparingly soluble, presumably polymeric, material derived from the sulfine was obtained. The products were those



21 **22** **23** **24**

Scheme 5 *Conditions:* i, *endo*-ester-*exo*-oxide in PhH at 80 °C, *exo*-ester-*exo*-oxide in PhMe at 111 °C; ii, *trans*-isomer at 60 °C and *cis*-isomer at 80 °C in PhH



25 **a**; R = H
b; R = Et
c; R = $[CH_2]_2CH=CH_2$

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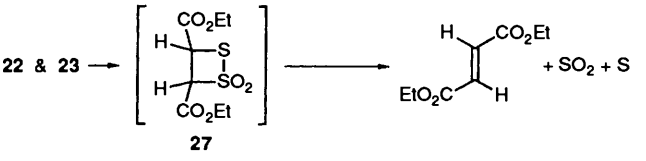
expected to arise from dimerisation[13] of the sulfine and subsequent decomposition[14] of the dimer **27** when the contents of the cold-trap were allowed to warm up (Scheme 6). Pyrolysis



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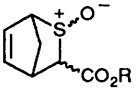
Scheme 6

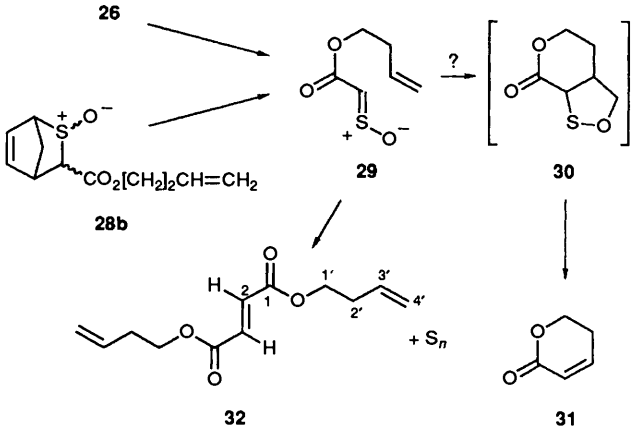
of the same mixture of the oxides **24** in benzene at 80 °C for 12 h gave essentially the same result; sulfur (46%) and diethyl fumarate (59%) were isolated, but this time a small amount (6%) of the cycloadduct **25b**[15] of anthracene and ethyl thioxoacetate was obtained. A little of the starting materials **24** (~10%) was recovered. The last experiment was repeated, under the same conditions, but with an equilibrium mixture of the sulfoxides **24** (*cis*:*trans* ratio ~1:10) obtained by base-catalysed epimerisation of the geometrical isomers. This time the products were sulfur (20%), diethyl fumarate (13%), and the deoxygenated cycloadduct **25b** (35%). The increased yield of the last product might reflect faster deoxygenation (by sulfur) of the *trans*-sulfoxide **24** than of the *cis*-sulfoxide. This would be expected if sulfur effected deoxygenation by initial bonding to oxygen, since the oxygen in the *trans*-sulfoxide would be less hindered. A control experiment showed that sulfur was able to deoxygenate the sulfoxides **24** under these conditions. Thus, when the 1:10 mixture **24** was heated with sulfur (2 mol equiv.) for only 2 h, the cycloadduct **25b** was obtained in 28% yield



28 **a**; R = $CH_2CH=CH_2$
b; R = $[CH_2]_2CH=CH_2$
c; R = $CH_2CH=CMe_2$
d; R = $[CH_2]_4CH=CH_2$

although only a small quantity of the sulfoxides **24** had otherwise decomposed. It is also possible that the transient sulfines **22** and **23** themselves undergo deoxygenation by sulfur and that the resulting ethyl thioxoacetate is then trapped by anthracene.

It was hoped that the sulfine **29**, or the corresponding *Z*-isomer, might undergo a novel, intramolecular dipolar cycloaddition to give the sultene **30**, under the conditions of high temperature and low pressure of FVP (Scheme 7). The required

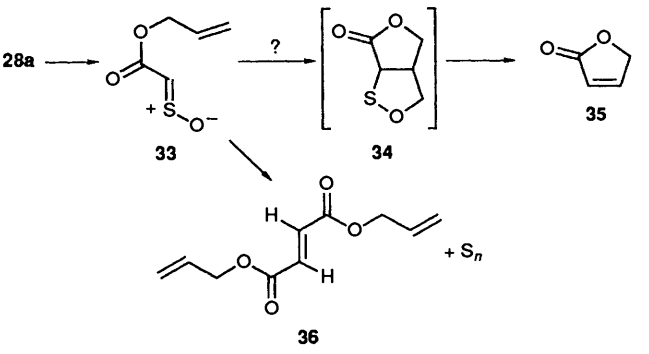


Scheme 7

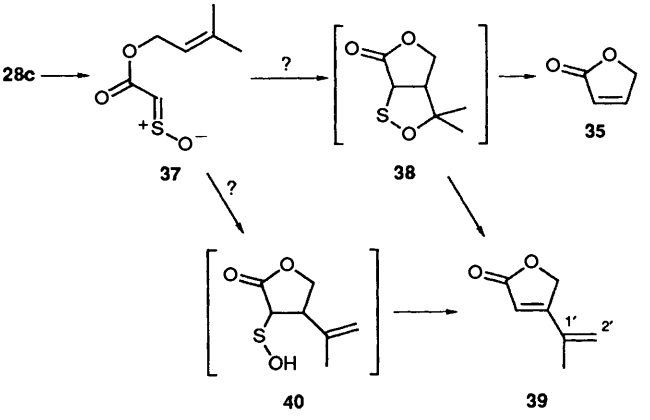
precursor, a *cis–trans* (~1:2.5) mixture of sulfoxides **26**, was prepared as usual from the cycloadduct **25c**. Initially, this mixture was heated under reflux in benzene for 15 h. As expected, the fumarate diester **32** was formed (40%), along with anthracene, but no other significant product was isolated. However, the same mixture **26**, when subjected to FVP at 500 °C, gave the fumarate **32** (43%), sulfur (58%), and the dihydropyrone **31** (13%). Each product was identified by comparison with authentic material, a reference sample of the diester **32** being prepared from fumaric acid and but-3-en-1-ol. The putative cyclisation to give the sultene **30** might occur more readily with the *E*-sulfine **29** than the *Z*-isomer. Therefore, the equilibrium mixture **26** (*cis*:*trans* ratio ~1:10) was pyrolysed at 500 °C, as before. The products isolated were the fumarate **32** (38%), sulfur (21%), and the dihydropyrone **31** (9%). Clearly, the stereochemistry of the sulfine had little, if any, effect upon the products; indeed, stereoisomerism of the sulfine may occur rapidly at 500 °C.

Similar products were obtained from the cyclopentadiene adducts **28b**, prepared as a mixture by oxidation of the corresponding mixture of thioaldehyde adducts **8b** and **9b**. The composition of the sulfoxide mixture **28b**, like those of the related sulfine precursors **28a**, **c** and **d**, was not examined in detail. However, by analogy with earlier studies[10] on the ethyl esters **21**, the major constituents must be the *exo* oxides of the *endo* and *exo* esters. Pyrolysis of the sulfoxides **28b** at 400 °C gave the fumarate **32** (40%) and no significant amount of the dihydropyrone **31**. At 500 °C, both the fumarate **32** (20%) and the dihydropyrone **31** (17%) were obtained, while at 600 °C the dihydropyrone **31** (37%) was the only significant product.

A related set of experiments was carried out to test the possible cyclisation of the allyl sulfine **33** (Scheme 8). When the appropriate mixture of cyclopentadiene cycloadducts **28a** was pyrolysed at 400 °C, the isolated products were sulfur (34%), the fumarate **36** (28%), and the furanone **35** (11%). Unexpectedly, the same furanone **35** was one of the products (33% yield) obtained from the prenyl sulfoxides **28c** at 500 °C, another being the isopropenyl derivative **39** (15%) (Scheme 9). None of the corresponding fumarate diester was detected in



Scheme 8



Scheme 9

the product mixture. Losses occurred during isolation of these volatile products, nevertheless their ratio in the crude reaction mixture was judged by ^{1}H NMR spectroscopy to be ~4:1, with the simple, and more volatile, furanone **35** as the major product. Although both furanones might conceivably have arisen from the same sultene **38**, an alternative path to the minor product **39** could pass through the sulfenic acid **40**. The putative transformation **37** ⟶ **40** resembles superficially the 'ene' reaction of the corresponding thioaldehyde, **3** ⟶ **4**. However, a concerted reaction of this novel type would require a pericyclic transition state involving 8 electrons in a 7-membered ring; an alternative, stepwise process might be more likely.

Finally, the precursors **28d** were pyrolysed to test whether a higher homologue of the sulfine **29** might undergo an 'ene' cyclisation strictly analogous to that of the corresponding thioaldehyde **10d**, that is to give a sulfoxide of the thialactone **11d**. However, at 500 °C, the cycloadducts **28d** gave di(hex-5-enyl) fumarate (54%) as the only significant product.

In conclusion, certain sulfines do indeed cyclise with C–C bond formation, but even in favourable cases the yields of cyclic products are low. The sultenes **30**, **34** and **38** may be formed initially, but the evidence for this is not substantial. Sultenes with five-membered rings[16] are stable at ordinary temperatures, but they have weak, and reactive, S–O bonds. Conceivably, at high temperatures, S–O bond cleavage in the putative intermediates might be followed by loss of sulfur and formaldehyde or acetone to yield the dihydropyrone **31** and the furanone **35**.

Experimental

General.—See our previous paper[1b] for details of instrumentation. NMR Spectra were obtained for solutions in deuteriochloroform; *J* values are in Hz. Analytical TLC was carried out on commercial, precoated, Merck silica gel GF_{254}

plates of thickness 0.25 mm. Compounds were revealed by UV light or iodine vapour. Column chromatography employed Merck silica gel HF_{254}, the flow being assisted with a water-pump.[17] Solutions in organic solvents were dried over sodium sulfate or magnesium sulfate and evaporated on a Büchi rotary evaporator. Light petroleum refers to the fraction boiling in the range 60–80 °C. When high boiling liquids were purified by Kugelrohr distillation, the cited 'b.p.' is the oven temperature not the equilibrium b.p.

Prop-2-enyl 2-Thiabicyclo[2.2.1]*hept-5-ene*-endo-3-*carboxylate* **8a** *and* -exo-3-*carboxylate* **9a**.—The carboxylic acids[1b,7] **6** and **7** (ratio ~7:3) (1.20 g, 7.7 mmol) in dichloromethane (8 cm^3) were stirred at room temperature with *N,N'*-carbonyldiimidazole (1.31 g, 8.1 mmol), with exclusion of moisture, for 3 h, during which time carbon dioxide was evolved. Solutions of prop-2-en-1-ol (0.45 g, 7.7 mmol) in dichloromethane (2 cm^3) and butyllithium (1.2 mmol) in tetrahydrofuran (THF) (1 cm^3) were mixed then added to the foregoing mixture, which was stirred overnight. The resulting mixture was diluted with dichloromethane (40 cm^3), washed successively with aq. sodium carbonate and water, and was dried and evaporated. The residue was chromatographed on a silica gel column. Elution with chloroform–light petroleum (1:4, then 1:1) gave the oily *endo*-ester **8a** (0.74 g, 49%); ν_{max}(liquid film)/cm^{-1} 1735; δ(90 MHz) 1.51–1.84 (m, 7-H_2), 3.81 (br s, 1- or 4-H), 4.12 (br s, 4- or 1-H), 4.47 (d, *J* 3, 3-H), 4.60 (d, *J* 6, with fine splitting, OCH_2), 5.16–5.53 (m, C=CH_2), 5.70–6.17 (m, 5- or 6-H and C*H*=CH_2) and 6.51 (dd, *J* 3 and 5, 6- or 5-H); and then the oily exo-*ester* **9a** (0.31 g, 21%) (Found: M^+, 196.0562. $C_{10}H_{12}O_2S$ requires M, 196.0558); ν_{max}(liquid film)/cm^{-1} 1735; δ(90 MHz) 1.67 and 1.93 (ABq, *J* 9, with fine splitting, 7-H_2), 3.34 (s, 3-H), 3.57 (br s, 1- or 4-H), 4.14 (br s, 4- or 1-H), 4.67 (d, *J* 5, with fine splitting, OCH_2), 5.17–5.54 (m, C=CH_2), 5.74–6.21 (m, 5- or 6-H and C*H*=CH_2) and 6.39 (dd, *J* 2.5 and 5.5, 6- or 5-H); together with a mixture of the endo- and exo-*esters* **8a** and **9a** (0.32 g, 21%), b.p. 70–75 °C (0.03 mbar, Kugelrohr distillation) (Found: C, 61.2; H, 6.3; S, 16.3. $C_{10}H_{12}O_2S$ requires C, 61.2; H, 6.1; S, 16.3%). The total yield of chromatographically pure esters was 91%.

But-3-enyl 2-Thiabicyclo[2.2.1]*hept-5-ene*-endo-3-*carboxylate* **8b** *and* -exo-3-*carboxylate* **9b**.—The carboxylic acids **6** and **7** (ratio ~1:1.3) (1.05 g, 6.7 mmol) and but-3-en-1-ol (0.48 g, 6.7 mmol) gave, as described for the esters **8a** and **9a**, the oily endo-*ester* **8b** (Found: M^+, 210.0710. $C_{11}H_{14}O_2S$ requires M, 210.0714); ν_{max}(liquid film)/cm^{-1} 1735; δ(90 MHz) 1.58–1.93 (m, 7-H_2), 2.38 (br q, 2'-H_2), 3.78 (br s, 1- or 4-H), 4.11 (br s, 4- or 1-H), 4.14 (t, *J* 6, OCH_2), 4.44 (d, *J* 3.5, 3-H), 5.10 (br d, *J* 11, CH=C*H*H), 5.13 (br d, *J* 17, CH=CH*H*), 5.57–6.12 (m, C*H*=CH_2), 5.89 (dd, *J* 2.5 and 5.0, 5- or 6-H) and 6.48 (dd, *J* 3.5 and 5.0, 6- or 5-H); the oily exo-*ester* **9b** (Found: M^+, 210.0707. $C_{11}H_{14}O_2S$ requires M, 210.0714); ν_{max}(liquid film)/cm^{-1} 1732; δ(90 MHz) 1.67 and 1.93 (ABq, *J* 9, with fine splitting, 7-H_2), 2.41 (br q, *J* 7, 2'-H_2), 3.31 (s, 3-H), 3.56 (br s, 1- or 4-H), 4.13 (br s, 4- or 1-H), 4.23 (t, *J* 7, OCH_2), 5.11 (br d, *J* 11, CH=C*H*H), 5.14 (br d, *J* 18, CH=CH*H*), 5.60–6.10 (m, 5- or 6-H and C*H*=CH_2) and 6.40 (dd, *J* 2.5 and 5.5, 6- or 5-H); and a mixture of the esters (total yield 80%).

Pent-4-enyl 2-Thiabicyclo[2.2.1]*hept-5-ene*-endo-3-*carboxylate* **8c** *and* -exo-3-*carboxylate* **9c**.—As described for the esters **8a** and **9a**, the carboxylic acids **6** and **7** and pent-4-en-1-ol gave the oily endo-*ester* **8c** (Found: M^+, 224.0868. $C_{12}H_{16}O_2S$ requires M, 224.0870; ν_{max}(liquid film)/cm^{-1} 1732; δ(90 MHz) 1.61–1.98 (m, 7- and 2'-H_2), 2.16 (br q, *J* 7, 3'-H_2), 3.79 (br s, 1- or 4-H), 4.12 (br t, *J* 7, OCH_2), 4.17 (m, 4- or 1-H), 4.46 (d, *J* 4, 3-H), 5.02 (br d, *J* 10, CH=C*H*H), 5.07 (br d, *J* 18, CH=CH*H*), 5.61–6.14 (m, C*H*=CH_2), 5.92 (dd, *J* 2.5 and 5.0, 5- or 6-H) and 6.51 (dd, *J* 3 and 5, 6- or 5-H); and the oily exo-*ester* **9c** (Found: M^+, 224.0887. $C_{12}H_{16}O_2S$ requires M, 224.0870); ν_{max}(liquid film)/cm^{-1} 1735; δ(90 MHz) 1.57–2.02 (m, 7- and 2'-H_2), 2.19 (br q, *J* 7, 3'-H_2), 3.32 (s, 3-H), 3.56 (br d, *J* 3, 1- or 4-H), 4.04–4.37 (m, 4- or 1-H), 4.20 (t, *J* 6, OCH_2), 5.02 (dd, *J* 2 and 9, CH=C*H*H), 5.07 (dd, *J* 2 and 18, CH=CH*H*), 5.62–6.10 (m, 5- or 6-H and C*H*=CH_2) and 6.41 (dd, *J* 2.5 and 5.5, 6- or 5-H) (combined yield 57%).

Hex-5-enyl 2-Thiabicyclo[2.2.1]*hept-5-ene*-endo-3-*carboxylate* **8d** *and* -exo-3-*carboxylate* **9d**.—As described for the esters **8a** and **9a**, the carboxylic acids **6** and **7**, and hex-5-en-1-ol, gave the oily endo-*ester* **8d** (Found: M^+, 238.1000. $C_{13}H_{18}O_2S$ requires M, 238.1027); ν_{max}(liquid film)/cm^{-1} 1733; δ(90 MHz) 1.26–1.88 (m, 7-, 2'- and 3'-H_2), 2.10 (br q, *J* 7, 4'-H_2), 3.79 (m, 4- or 1-H), 4.08 (m, 1- or 4-H), 4.11 (t, *J* 6, OCH_2), 4.46 (d, *J* 3.5, 3-H), 4.99 (br d, *J* 11, CH=C*H*H), 5.03 (br d, *J* 19, CH=CH*H*), 5.60–6.09 (m, 5- or 6-H and C*H*=CH_2) and 6.51 (dd, *J* 3 and 5.5, 6- or 5-H); and the oily exo-*ester* **9d** (Found: M^+, 238.1034. $C_{13}H_{18}O_2S$ requires M, 238.1027); ν_{max}(liquid film)/cm^{-1} 1734; δ(90 MHz) 1.20–2.32 (m, 7-, 2'-, 3'- and 4'-H_2), 3.32 (s, 3-H), 3.57 (br d, *J* 2, 1- or 4-H), 4.18 (m, 4- or 1-H), 4.20 (t, *J* 6, OCH_2), 5.00 (br d, *J* 10, CH=C*H*H), 5.04 (br d, *J* 18.5, CH=CH*H*), 5.60–6.10 (m, 5- or 6- and C*H*=CH_2) and 6.42 (dd, *J* 2.5 and 5.5, 6- or 5-H) (combined yield 79%).

Hept-6-enyl 2-Thiabicyclo[2.2.1]*hept-5-ene*-endo- *and* -exo-3-*carboxylate* **8e** *and* **9e**.—As described for the esters **8a** and **9a**, a mixture of the acids **6** and **7** (~4:1), and hept-6-en-1-ol,[18] gave an oily mixture of the *endo*- **8e** and *exo*-ester **9e** (~3:2 after chromatography). The mixture was purified, but not separated, by chromatography on a silica gel column, as before; δ(90 MHz) 0.80–1.90 (m, 7-, 2'-, 3'- and 4'-H_2, *endo* and *exo*), 2.10 (br q, *J* 7, 5'-H_2, *endo* and *exo*), 3.22 (s, 3-H, *exo*), 3.55 (br s, 1- or 4-H, *exo*), 3.77 (br s, 1- or 4-H, *endo*), 4.0–4.2 (m, OCH_2 and 4- or 1-H, *endo* and *exo*), 4.42 (d, *J* 3.5, 3-H, *endo*), 4.90–5.10 (m, C=CH_2, *endo* and *exo*), 5.60–6.00 (m, 5- or 6-H and C*H*=CH_2, *endo* and *exo*) and 6.35–6.55 (m, 6- or 5-H, *endo* and *exo*).

Flash Vacuum Pyrolysis (*FVP*). *General Methods*.—Pyrolyses were carried out in a horizontal silica tube (2.5 × 55 cm) at 400–600 °C and 10^{-3}–10^{-5} mbar. Cycloadducts were volatilised in a Büchi Kugelrohr oven at 50–180 °C; often they were first deposited on Celite to aid evaporation. Volatile products were collected in a U-tube cooled in liquid nitrogen. For further details see our previous paper.[1b] The oily thia-alkenolides **11** were generally formed as mixtures with white solids, believed to be polymers of the corresponding thioaldehydes which had survived pyrolysis. The solids were insoluble in common solvents and therefore easily separated from the oils. When cycloadducts of anthracene were pyrolysed, anthracene was deposited on the cool section of the pyrolysis tube between the furnace and the trap.

Preparation of 3-*Thiahex-5-en-6-olide* **11a** *by FVP*.—The cyclopentadiene adducts **8a** and **9a** (~3:2) (300 mg), deposited on Celite, were volatilised at 60 °C and 5 × 10^{-3} mbar, the vapours passing through the pyrolysis tube at 500 °C during 15 min. Chromatography of the products on silica plates developed with ethyl acetate–hexane (1:5) gave the *thiahexenolide* **11a** as a yellow oil (120 mg, 60%) (Found: M^+, 130.0091. $C_5H_6O_2S$ requires M, 130.0089); ν_{max}(liquid film)/cm^{-1} 1760; δ_H(200 MHz) 3.27 (dd, *J* 8.0 and 0.8, 4-H_2), 3.30 (s, 2-H_2), 5.56 (td, *J* 7.8 and 5.8, 5-H) and 6.48 (dt, *J* 5.7 and 0.8, 6-H); δ_C(50.4

MHz) 22.9 (C-4), 29.4 (C-2), 111.1 (C-5), 141.5 (C-6) and 167.8 (C-1).

Methyl 5-Formyl-3-thiapentanoate **12**.—The thiahexenolide **11a** was stirred in methanol with silica gel at room temperature for 2 h to form the *aldehydo ester* **12** as an oil (Found: M^+, 162.0346. $C_6H_{10}O_3S$ requires M, 162.0350); ν_{max}(liquid film)/cm^{-1} 1732; δ(90 MHz) 2.62–3.09 (m, 4- and 5-H_2), 3.27 (s, 2-H_2), 3.77 (s, OMe) and 9.76 (t, *J* 1.5, 6-H).

Preparation of 3-Thiahept-5-en-7-olide **11b** *and 5-Vinyl-3-thiapentan-5-olide* **13** *by FVP*.—The cyclopentadiene adducts **8b** and **9b** (~7:5) (260 mg), deposited on Celite, were volatilised at 50 °C and 10^{-4} mbar, and pyrolysed at 500 °C during 25 min. Chromatography of the products on silica plates, as before, gave the cycloadducts **8b** and **9b** (30 mg, 12%), the oily *thiaheptenolide* **11b** (24 mg, 13%) (Found: M^+, 144.0234. $C_6H_8O_2S$ requires M, 144.0245); ν_{max}(CCl_4)/cm^{-1} 1760; δ_H(200 MHz) 3.17 (s, 2-H_2), 3.40 (d, *J* 8.1, with fine splitting, 4-H_2), 4.74 (m, 7-H_2), 5.57 (dt, *J* 11.2 and 2.8, 6-H) and 5.67 (dtt, *J* 11.2, 8.4 and 1.8, 5-H); δ_C(50.4 MHz) 29.3 (CH_2), 32.0 (CH_2), 63.6 (C-7), 127.1 (CH), 128.2 (CH) and 169.8 (C-1); and the oily *thiapentanolide* **13** (52 mg, 29%) (Found: M^+, 144.0249. $C_6H_8O_2S$ requires M, 144.0245); ν_{max}(CCl_4)/cm^{-1} 1765, 1750 and 1715 (all strong); ν_{max}($CHCl_3$)/cm^{-1} 1750sh and 1738; δ_H(200 MHz) 2.85 (dd, *J* 12.4 and 10.5, 4-H), 2.96 (ddt, *J* 12.2, 3.4 and 0.7, 4-H), 3.23 (dd, *J* 14.9 and 0.7, 2-H), 3.56 (dd, *J* 14.9 and 0.4, 2-H), 4.89–5.00 (m, 5-H), 5.32 (dt, *J* 10.5 and 1.0, 2′-H), 5.42 (ddd, *J* 17.2, 1.3 and 1.0, 2′-H) and 5.89 (ddd, *J* 17.2, 10.5 and 5.8, 1′-H); δ_C(50.4 MHz) 26.0 (CH_2), 29.4 (CH_2), 79.1 (C-5), 118.7 (C-2′), 133.6 (C-1′) and 167.3 (C-1).

When the adducts **8b** and **9b** were pyrolysed at 400 °C the major product was the thiaheptenolide **11a** (14%), accompanied by the cycloadducts **8b** and **9b** (28%) and only a trace of the thiapentanolide **13**, whereas pyrolysis at 600 °C gave exclusively the thiapentanolide **13** (34%).

Preparation of 3-Thiaoct-5-en-8-olide **11c** *by FVP*.—The cyclopentadiene adducts **8c** and **9c** (~1:1) (250 mg) were volatilised at 100 °C and 10^{-4} mbar, and pyrolysed at 500 °C during 15 min. Chromatography of the products, as before, gave the *thiaoctenolide* **11c** as a yellow oil (100 mg, 57%) (Found: M^+, 158.0404. $C_7H_{10}O_2S$ requires M, 158.0402); ν_{max}(liquid film)/cm^{-1} 1745; ν_{max}(CCl_4)/cm^{-1} 1752; δ_H(200 MHz) 2.34 (ddd, *J* 8.1, ~5 and ~6, 7-H_2), 3.17 (s, 2-H_2), 3.30 (d, *J* 7.5, 4-H_2), 4.16 (t, *J* 5.2, 8-H_2) and 5.48 and 5.59 (tABq, *J* 8.1 and 11.0, 5- and 6-H); δ_C(50.4 MHz) 28.0 (CH_2), 28.3 (CH_2), 31.5 (CH_2), 59.9 (C-8), 123.7 (CH), 132.0 (CH) and 170.2 (C-1), together with weak signals at 29.8 (CH_2), 30.8 (CH_2), 33.9 (CH_2), 60.5 (CH_2), 129.3 (CH), 131.9 (CH) and 171.1 (C).

Preparation of (Z)- *and* (E)-3-*Thianon-5-en-9-olide* **11d** *by FVP*.—The cyclopentadiene adducts **8d** and **9d** (~3:2) (330 mg) were volatilised at 150 °C and 6×10^{-5} mbar, and pyrolysed at 500 °C during 20 min. Chromatography of the products, as before, gave the stereoisomeric *thianonenolides* **11d** (*Z*:*E* ~1:2) (150 mg, 63%), m.p. 34 °C (from light petroleum) (Found: C, 55.8; H, 6.9%; M^+, 172.0557. $C_8H_{12}O_2S$ requires C, 55.5; H, 7.0%; M, 172.0557); ν_{max}(CCl_4)/cm^{-1} 1748; δ_H(200 MHz) 1.61–2.28 (m, 7- and 8-H_2), 2.97–3.36 (m, 2- and 4-H_2), 3.73 (br dt, *J* 11.8 and ~3, 9-H, *E*-isomer), 4.18 (t, *J* 6.2, 9-H_2, *Z*-isomer), 4.98 (td, *J* 11.5 and 2.0, 9-H, *E*-isomer), 5.42 (m, 5- and 6-H, *Z*-isomer), 5.44 (dddd, *J* 15.5, 10.5, 3.7 and 1.7, 5- or 6-H, *E*-isomer) and 5.61 (dddd, *J* 15.1, 10.1, 3.4 and 1.2, 6- or 5-H, *E*-isomer); δ_C(50.4 MHz) (*E*-isomer) 28.4 (CH_2), 31.4 (CH_2), 34.6 (CH_2), 37.0 (CH_2), 65.4 (C-9), 125.6 (CH), 135.5 (CH) and 173.1 (C-1); δ_C(50.4 MHz) (*Z*-isomer) 22.6 (CH_2), 25.1 (CH_2), 29.4 (CH_2), 34.2 (CH_2), 63.1 (C-9), 128.2 (CH), 129.3 (CH) and 170.9 (C-1). The isomers were not separable by chromatography on silica plates or by recrystallisation (the 1:2 mixture formed large plates).

3-*Thianonan-9-olide* **14**.—The foregoing thianonenolides **11d** (90 mg, 0.53 mmol) were stirred in methanol (10 cm^3) with dipotassium azodicarboxylate (1.0 g) at room temperature. A mixture of methanol, acetic acid, and water (1:1:1) (3 cm^3) was added slowly, dropwise, until the yellow colour of the azo compound had disappeared. The mixture was diluted with water and extracted with diethyl ether. The extracts were dried and evaporated. The residue was chromatographed on silica plates to give the oily *thianonanolide* **14** (60 mg, 66%) (Found: M^+, 174.0708. $C_8H_{14}O_2S$ requires M, 174.0714); δ_H(90 MHz) 1.48–1.95 (m, 5-, 6-, 7- and 8-H_2), 2.72 (t, *J* 6, 4-H_2), 3.22 (s, 2-H_2) and 4.32 (t, *J* 5, 9-H_2); and the thianonenolides **11d** (24 mg, 27%) consisting mainly of the *E*-isomer.

Preparation of (Z)- *and* (E)-3-*Thiadec-5-en-10-olide* **11e** *by FVP and its Reduction to 3-Thiadecan-10-olide*.—The cyclopentadiene adducts **8e** and **9e** (3:2) (310 mg) were volatilized at 150 °C and 9×10^{-5} mbar, and pyrolysed at 500 °C during 15 min. Chromatography of the products, as before, gave the *thiadecenolides* **11e** (*Z*:*E* ~ 1:2; the assignment of configurations is tentative) (150 mg, 66%) (Found: M^+, 186.0708. $C_9H_{14}O_2S$ requires M, 186.0715); ν_{max}(CCl_4)/cm^{-1} 1742; δ_H(200 MHz) 1.54–1.78 (m, 8- and 9-H_2), 1.93–2.04 (m, 7-H_2, *E*-isomer), 2.24–2.35 (m, 7-H_2, *Z*-isomer), 3.12–3.33 (m, 2- and 4-H_2), 4.09 (t, *J* 5.5, 10-H_2, *E*-isomer), 4.18 (m, 10-H_2, *Z*-isomer) and 5.21–5.55 (m, 5- and 6-H); δ_C(50.4 MHz; *E*-isomer) 25.7 (CH_2), 27.2 (CH_2), 33.9 (CH_2), 35.4 (CH_2), 37.3 (CH_2), 67.1 (C-10), 126.3 (CH), 135.0 (CH) and 172.4 (C-1); δ_C(50.4 MHz; *Z*-isomer) 25.3 (CH_2), 25.5 (CH_2), 27.9 (CH_2), 30.3 (CH_2), 35.1 (CH_2), 66.8 (C-10), 127.4 (CH), 131.4 (CH) and 170.9 (C-1).

Reduction of the thiadecenolides **11e** with diimide, as described for the thianonenolides **11d**, gave 3-*thiadecan-10-olide* (33%) as an oil (Found: M^+, 188.0861. $C_9H_{16}O_2S$ requires M, 188.0871); δ(90 MHz) 1.40–1.95 (m, 5-, 6-, 7-, 8- and 9-H_2), 2.80 (br t, *J* 6, 4-H_2), 3.16 (s, 2-H_2) and 4.25 (t, *J* 5, 10-H_2); together with recovered thiadecenolides **11e** (44%) (*Z*:*E* ~ 1:1).

Conversion of the Thianonenolide **11d** *into 3-Vinylhex-2-en-6-olide* **20** via *the Intermediates* **16**, **17**, **18** *and* **19** (*Scheme* 4).—The thianonenolide **11d** (160 mg, 0.93 mmol) and triethyloxonium tetrafluoroborate (190 mg, 1 mmol) were stirred in dichloromethane (15 cm^3) at room temperature for 2 h. The mixture was evaporated and the residual sulfonium salt **16** was stirred in dry acetonitrile (2 cm^3) under nitrogen at 0 °C. DBN (148 mg, 1.2 mmol) was added dropwise and the mixture was stirred for 20 min. The mixture was added to water (10 cm^3) and extracted with diethyl ether. The extracts were washed successively with dil. hydrochloric acid and brine, then were dried by passage through anhydrous sodium sulfate. The mixture was evaporated and the residue was chromatographed on silica plates developed with hexane–diethyl ether (9:1) to give 2-ethylthio-3-vinylhexan-6-olide **18** (152 mg, 82%) as an oil, judged by the following NMR spectra to consist largely of a single, probably *trans*, diastereoisomer; δ_H(200 MHz) 1.25 (t, *J* 7.4, Me), 1.65–2.05 (m, 4- and 5-H_2), 2.62 (q, *J* 7.4, SCH_2), 2.67 (m, 3-H), 3.76 (d, *J* 2.1, 2-H), 4.22 (ddd, *J* 12.0, 5.0 and ~1, 6-H), 4.88 (dd, *J* 12.0 and 9.0, with fine splitting, 6-H), 5.10 (dt, *J* 10.3 and 1.2, 2′-H), 5.14 (dt, *J* 17.2 and 1.2, 2′-H) and 5.90 (ddd, *J* 17.2, 10.3 and 7.2, 1′-H); together with weak signals possibly arising from the *cis*-isomer, 1.27 (t, *J* 7.4, Me), 3.81 (d, *J* 5.8, 2-H) and ~5.2 (m, 2′-H); δ_C(50.4 MHz) 14.3 (Me), 26.8 (CH_2S), 28.6 (C-4 or -5), 30.4 (C-5 or -4), 41.9 (C-3), 54.7 (C-2), 68.9 (C-6), 116.1 (C-2′), 139.0 (C-1′) and 171.9 (C-1); *m*/*z* 200 (M^+).

The hexanolide **18** (140 mg, 0.7 mmol) was treated with peracetic acid (29% w/v in acetic acid; 0.78 mmol) in dichloromethane (10 cm^3) at room temperature for 1 h. The mixture was washed successively with aq. sodium hydrogen carbonate and water, and was then dried and evaporated to give an oily mixture (~2:1) of the stereoisomeric sulfoxides **19** (142 mg, 94%); δ_H(90 MHz) 1.38 (t, *J* 7, Me, minor isomer), 1.41 (t, *J* 7, Me, major isomer), 1.62–2.45 (m, 4- and 5-H_2), 2.55–3.25 (m, SCH_2), 3.30–3.65 (m, 3-H), 3.77 (d, *J* 2, 2-H, major isomer), 4.05 (d, *J* 2, 2-H, minor isomer), 4.20–4.72 (m, 6-H_2), 5.15–5.55 (m, 2′-H_2) and 5.65–6.15 (m, 1′-H). These sulfoxides **19** (190 mg) were volatilised (150 °C; 3 × 10^{-4} mbar) through an FVP tube (see above) at 500 °C during 15 min. Chromatography of the products on silica plates gave *3-vinylhex-2-en-6-olide* **20** as an oil (67 mg, 55%) (Found: M^+, 138.0684. $C_8H_{10}O_2$ requires M, 138.0681); $\nu_{max}(CCl_4)/cm^{-1}$ 1730 and 1710; δ_H(200 MHz) 2.04–2.17 (m, 5-H_2), 2.58 (t, *J* 7.0, with fine splitting, 4-H_2), 4.25 (m, 6-H_2), 5.38 (d, *J* 10.7, with fine splitting, 2′-H), 5.58 (d, *J* 17.5, 2′-H), 5.96 (dd, *J* 1.4 and 0.7, 2-H) and 6.41 (dd, *J* 17.5 and 10.7, 1′-H); δ_C(50.4 MHz) 26.1 (C-4 or -5), 26.2 (C-5 or -4), 66.8 (C-6), 119.4 (C-2′), 121.5 (C-2), 138.5 (C-1′), 149.2 (C-3) and 169.6 (C-1).

Alternatively, the sulfoxides **19** were heated under reflux, under nitrogen, in benzene containing calcium carbonate for 24 h. Chromatography of the reaction mixture gave the hexenolide **20** (40%) and a mixture of the sulfoxides **19** (38%) consisting largely of the original major isomer. When the mixture of sulfoxides was heated for a further 20 h in *toluene* under reflux, a further quantity (18%) of the hexenolide **20** was obtained.

Preparation of the Sulfoxides **24** *and* **26** *of Anthracene Cycloadducts.*—The preparation of the ethyl ester sulfoxides **24** was reported earlier.[10] In the present study generally, peracetic acid was preferred as oxidant, as exemplified by the following preparation of the butenyl derivatives **26**. The carboxylic acid[1b,15] and but-3-en-1-ol with *N,N′*-carbonyldiimidazole gave, as described for the esters **8a** and **9a**, the but-3-enyl ester **25c**; δ_H(90 MHz) 2.30 (br q, *J* 6.5, 2′-H_2), 4.05 (t, *J* 6.5, OCH_2), 4.08 (d, *J* 2, 12-H), 4.91–5.22 (m, 4′-H_2 and 9- and 10-H), 5.47–6.0 (m, 3′-H) and 7.07–7.50 (m, ArH).

This sulfide **25c** (0.40 g, 1.24 mmol) and peracetic acid (29% w/v in acetic acid; 1.3 mmol) in dichloromethane (15 cm^3) were kept at room temperature until the oxidation was complete (*ca.* 1 h, TLC monitoring). The mixture was washed successively with aq. sodium hydrogen carbonate and water, then was dried and evaporated to give the sulfoxides **26** (414 mg, 99%) as a mixture of *cis*- and *trans*-*S*-oxides (~1:2.5) sufficiently pure for the pyrolysis experiments; δ_H(90 MHz) 2.30 (br q, *J* 6.5, 2′-H_2), 3.12 (d, *J* 2, 12-H, *trans*-isomer), 3.90 (d, *J* 2, 12-H, *cis*-isomer), 4.10 (t, *J* 6.5, OCH_2), 4.80–5.20 (m, 4′-H_2 and 9-H), 5.30–5.90 (m, 3′-H), 5.68 (s, 10-H, *trans*-isomer), 5.75 (s, 10-H, *cis*-isomer) and 7.10–7.70 (m, ArH). Attempts at chromatographic purification caused loss of material. This mixture of sulfoxides **26** was treated at room temperature with triethylamine (2 mol dm^{-3}) in benzene for 12 h to give the corresponding equilibrium mixture, *cis*:*trans* ~ 1:10 as measured from the NMR signals at δ 3.12 and 3.90.

Preparation of the Sulfoxides **28** *of Cyclopentadiene Cycloadducts.*—Generally, mixtures of the *endo*- **8** and *exo*- **9** cycloadducts were treated in dichloromethane with 1 mol equiv. of peracetic acid, as described for the preparation of the sulfoxides **26**. The prenyl derivatives **28c** were obtained likewise from the corresponding *endo*- and *exo*-sulfides.[1b] Generally, mixtures of epimeric sulfoxides were formed, as reported[10] for the oxidation of the *endo*- and *exo*-cycloadducts of ethyl thioxoacetate. These mixtures **28** were used directly in the pyrolysis experiments. By analogy with the ethyl thioxoacetate derivatives, the major diastereoisomers present are believed to be the *exo*-sulfoxides of both the *endo*- and *exo*-esters. However, the ^1H NMR spectra indicated the presence of at least one other diastereoisomer.

Pyrolysis of the Anthracene Cycloadduct Sulfoxides **24**.—A mixture of the *cis* and *trans* (~1:2.5) sulfoxides[10] **24** (340 mg), deposited on Celite, was volatilised at 150 °C and 6 × 10^{-5} mbar, and pyrolysed at 500 °C during 15 min. Chromatography of the products on silica plates developed with diethyl ether–hexane (1:4) gave sulfur (18 mg, 52%) and diethyl fumarate (60 mg, 64%). Alternatively, the same mixture **24** (340 mg) was heated under reflux in dry benzene (15 cm^3) under nitrogen for 12 h. The mixture was evaporated and the residue was triturated with methanol (5 cm^3) and set aside to allow most of the anthracene to crystallise out. The mixture was filtered and the filtrate was evaporated. Chromatography of the residue, as before, gave sulfur (16 mg, 46%), diethyl fumarate (55 mg, 59%) and the cycloadduct **25b** (20 mg, 6%). A quantity of the sulfoxides **24** (~10%) was also recovered from the silica plate. Similarly, the equilibrium mixture (*cis*:*trans* ~ 1:10) of sulfoxides **24** (390 mg) was heated in benzene (15 cm^3) under reflux, under nitrogen, for 12 h. The usual work-up gave sulfur (20%), diethyl fumarate (13%) and the cycloadduct **25b** (35%). When the same equilibrium mixture **24** (156 mg) was heated under reflux in benzene (10 cm^3) with sulfur (32 mg) for 2 h, the cycloadduct **25b** was obtained in 28% yield.

Pyrolysis of the Anthracene Cycloadduct Sulfoxides **26**.—The sulfoxides **26** (*cis*:*trans* 1:2.5) (460 mg), deposited on Celite, were volatilised at 160 °C and 6 × 10^{-5} mbar, and pyrolysed at 500 °C during 15 min. The usual work-up gave sulfur (58%), dibut-3-enyl fumarate **32** (43%) and the dihydropyrone **31** (13%). The last product was extracted from the 'loading band' (R_f ~0) of the silica plates with dichloromethane and was purified by rechromatography in diethyl ether. It was identified by comparison of its IR and ^1H NMR spectra with those of a commercial (Aldrich Chemical Company Ltd.) sample. *Dibut-3-enyl fumarate* **32**, prepared also from but-3-enol and fumaric acid, formed an oil (Found: M^+, 224.1040. $C_{12}H_{16}O_4$ requires M, 224.1049); $\nu_{max}(CCl_4)/cm^{-1}$ 1728; δ_H(200 MHz) 2.42 (qt, *J* 6.7 and 1.3, 2′-H_2), 4.24 (t, *J* 6.7, 1′-H_2), 5.07 (dm, *J* 10.2, 4′-H), 5.12 (dq, *J* 17.2 and 1.7, 4′-H), 5.78 (ddt, *J* 17.2, 10.2 and 6.7, 3′-H) and 6.82 (s, 2-H); δ_C(50.4 MHz) 32.9 (C-2′), 64.3 (C-1′), 117.6 (C-4′), 133.6 (C-2 and -3′) and 164.9 (C=O). This experiment was repeated but with the equilibrium mixture (*cis*:*trans* ~ 1:10) of sulfoxides **26**; the products were sulfur (21%), dibut-3-enyl fumarate (38%) and the dihydropyrone **31** (9%).

Alternatively, the sulfoxides **26** (*cis*:*trans* ~ 1:2.5) (150 mg) were heated under reflux in benzene (15 cm^3), under nitrogen, for 15 h. The usual work-up gave the fumarate **32** (20 mg, 40%), along with anthracene.

Pyrolysis of the Cyclopentadiene Cycloadduct Sulfoxides **28**.—A mixture of the diastereoisomeric allyl sulfoxides **28a** (430 mg), deposited on Celite, was volatilised at 160 °C and 6 × 10^{-5} mbar, and pyrolysed at 400 °C during 15 min. The products were chromatographed on silica plates developed with diethyl ether–hexane (1:9) to give sulfur (22 mg, 34%) and diprop-2-enyl fumarate **36** (55 mg, 28%). Extraction of the 'loading band' (R_f ~0) of the plates with dichloromethane and rechromatography of the extract in diethyl ether gave the furanone **35** (18 mg, 11%), which was identified by comparison of its IR and ^1H NMR spectra with those of a commercial (Aldrich Chemical Company Ltd.) sample.

Similarly, the but-3-enyl sulfoxides **28b** (330 mg), deposited on Celite, were volatilised at 180 °C and 1 × 10^{-4} mbar, and

pyrolysed at 500 °C during 25 min. The products, dibut-3-enyl fumarate **32** (32 mg, 20%) and the dihydropyranone **31** (25 mg, 17%) were identified as described for the pyrolysis of the anthracene derivatives **26**. When the pyrolysis was repeated but at 600 °C, the dihydropyranone **31** was obtained (37%) as the only identified product. Conversely, with a pyrolysis temperature of 400 °C only dibut-3-enyl fumarate (40%) was isolated.

The prenyl sulfoxides **28c** (260 mg), deposited on Celite, were volatilised at 150 °C and 8×10^{-5} mbar, and pyrolysed at 500 °C to give a mixture of the furanone **35** and its isopropenyl derivative **39** (ratio ~4:1 as judged by ^{1}H NMR spectroscopy). Chromatography on silica plates developed with diethyl ether gave 4-*isopropenylfuran*-2(5H)-*one* **39** (20 mg, 15%) (Found: M^+, 124.0523. $C_7H_8O_2$ requires M, 124.0524); ν_{max}-(CCl_4)/cm^{-1} 1789, 1729 and 1690; δ_H(200 MHz) 2.02 (dd, *J* 1.5 and 0.9, Me), 4.98 (d, *J* 1.7, 5-H_2), 5.29 (m, 2′-H), 5.35 (m, 2′-H) and 5.95 (t, *J* 1.7, 3-H); δ_C(50.4 MHz) 20.05 (Me), 70.8 (C-5), 114.6 (C-3), 119.8 (C-2′), 135.5 (C-1′), 164.3 (C-4) and 173.9 (C-2); and the furanone **35** (29 mg, 33%). Substantial loss of the volatile furanone **35** occurred during chromatographic purification.

The hex-5-enyl sulfoxides **28d** (250 mg), deposited on Celite, were volatilised at 80 °C and 1×10^{-4} mbar, and pyrolysed at 500 °C during 20 min. The only product isolated after chromatography was *dihex-5-enyl fumarate* (72 mg, 54%) [Found: M^+, 252.1723. $C_{16}H_{24}O_4$ requires (*M* − CO), 252.1726]; ν_{max}(CCl_4)/cm^{-1} 1727; δ(90 MHz) 1.20–1.95 (m, 2′- and 3′-H_2), 2.00–2.28 (m, 4′-H_2), 4.20 (t, *J* 6, 1′-H_2), 4.96 (d, *J* 10, 6′-H), 5.01 (d, *J* 17, 6′-H), 5.55–6.05 (m, 5′-H) and 6.85 (s, 2-H).

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