The Transient Dienophile Diethyl Thioxomalonate and its *S*-Oxide (Sulphine) Formed by Retro-Diels–Alder Cleavage Reactions

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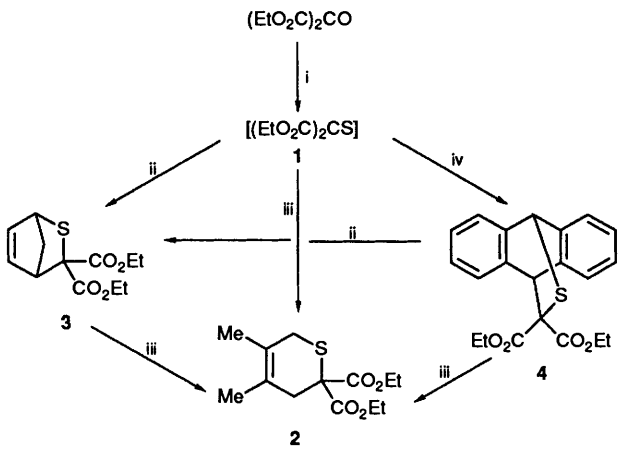
Diels–Alder adducts **3** and **4** of diethyl thioxomalonate **1**, formed from diethyl oxomalonate (mesoxalate) and phosphorus pentasulphide, with cyclopentadiene and anthracene, dissociate at 111 °C to release the reactive thioketone **1**. This was trapped *in situ* with 2,3-dimethylbuta-1,3-diene to give the corresponding cycloadduct **2**. Similarly, the thioketone **1** reacted with 2-trimethylsiloxybuta-1,3-diene **8** to form only the 5-trimethylsiloxythiine **13**, and with β-pinene **16** to form only one 'ene' product **17b**, with C–S bond formation. The *S*-oxide **19** of the anthracene adduct **4** and the *exo*-*S*-oxide **27** of the cyclopentadiene adduct **3** likewise dissociated thermally to release the corresponding sulphine, diethyl thioxomalonate *S*-oxide **21**, which was trapped *in situ* as the dimethylbutadiene adduct **23**. The *exo*-sulphoxide **27**, when heated alone, gave the sultene **29**, presumably *via* [2,3]-sigmatropic rearrangement of the transient *endo*-sulphoxide **28**. The sulphine **21**, generated by flash vacuum pyrolysis of the anthracene adduct **19**, reacted at low temperature with cyclopentadiene to give the *exo*-sulphoxide **27**, and with water to give diethyl malonate.

We showed that the Diels–Alder adducts of ethyl thioxoacetate, EtO_2CCHS, with anthracene[1] and cyclopentadiene[2] dissociate when heated and thereby serve as convenient auxiliary precursors for this labile thioaldehyde. Similarly, the corresponding *S*-oxides of the cycloadducts dissociate thermally to liberate the *Z* and *E* isomers of the labile sulphine, ethyl thioxoacetate *S*-oxide.[3] We report now the formation of the electrophilic dienophiles diethyl thioxomalonate **1** (Scheme 1) and its *S*-oxide **21** (Scheme 4) by retro-Diels–Alder cleavage of their anthracene and cyclopentadiene cycloadducts.

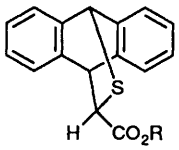


Scheme 1. *Co-reactants*: i, P_4S_{10}; ii, cyclopentadiene; iii, 2,3-dimethylbuta-1,3-diene; iv, anthracene.

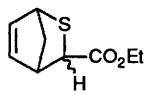
Beelitz *et. al*,[4] formed diethyl thioxomalonate **1** from diethyl dibromomalonate and potassium ethyl xanthate in acetone. The transient thioketone was trapped *in situ* with 2,3-dimethylbuta-1,3-diene to give the cycloadduct **2** in good yield. Using the same reactants, but with an excess of cyclopentadiene as the trapping agent, we obtained the required cycloadduct **3**. However, this method failed to yield any detectable amount of the cycloadduct **4** when anthracene replaced dimethylbutadiene or cyclopentadiene, no doubt on account of the relatively low reactivity of anthracene in Diels–Alder reactions and its low solubility in acetone. In a different approach (Scheme 1), diethyl oxomalonate(mesoxalate) was treated with phosphorus pentasulphide (P_4S_{10}).† In preliminary experiments, carried out by Miss M. C. McGuire, the oxomalonate and phosphorus pentasulphide were heated in benzene or tetrahydrofuran (THF) in the presence of anthracene. The cycloadduct **4** was obtained as a white, crystalline compound, but in consistently poor (< 15%) yield. Some improvement in yield was obtained with the Lawesson reagent, [5] but the product **4** was then more difficult to purify. However, when diethyl oxomalonate and anthracene (3 mol equiv.) were heated in dry pyridine at 70–80 °C in the presence of phosphorus pentasulphide (0.4 mol equiv.), the cycloadduct **4** was obtained in better yield (20–25% after purification). This was acceptable since all the reactants were readily available. The same method gave good yields of the cycloadducts **2**[4] and **3**. Treatment of the diester **4** with aqueous sodium hydroxide caused hydrolysis and decarboxylation to give the monoacid **5**. This was identical with material obtained by hydrolysis of the cycloadduct **6**[1] of anthracene and ethyl thioxoacetate. In general, cycloadducts of diethyl thioxomalonate are the synthetic equivalents of those of ethyl thioxoacetate. For example, in an alternative approach to the synthesis of the cycloadduct **3**, Professor G. El Naggar treated diethyl bromomalonate with sodium thiosulphate to form the corresponding Bunte salt, $(EtO_2C)_2CHS_2O_3Na$. As expected,[2] this underwent elimination of sulphite dianion in the presence of triethylamine and calcium chloride to give the thioketone **1**, which was trapped *in situ* with cyclopentadiene. However, the resulting cycloadduct **3** was accompanied by the known[2] *endo* and *exo* monoesters **7**. The decarboxylation observed under these mild, basic conditions may be assisted by the α thio substituent.

Both the cycloadducts **3** and **4** are stable when heated alone in toluene under reflux (*ca.* 111 °C). After 24 h the cyclopentadiene adduct **3** was essentially unchanged and the anthracene adduct

† This method was first suggested to us by Professor J. K. Sutherland (University of Manchester); see also C. M. Bladon, I. E. G. Ferguson, G. W. Kirby, A. W. Lochead and D. C. McDougall, *J. Chem. Soc., Chem. Commun.*, 1983, 423.



5 R = H
6 R = Et



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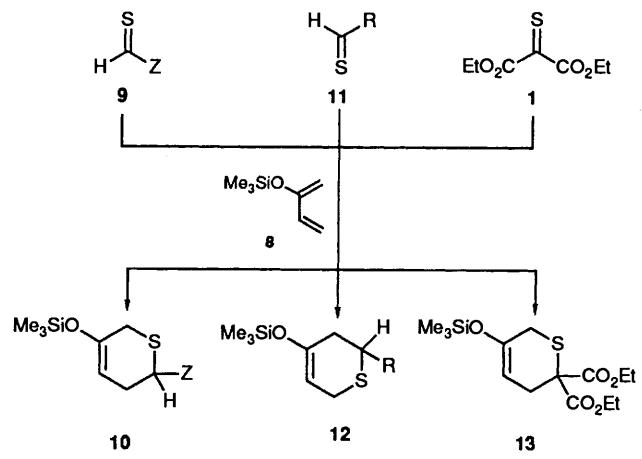
4 was recovered in 75% yield. However, both cycloadducts dissociate readily under these conditions. Thus, when the anthracene adduct **4** was heated for 1 h with dimethylbutadiene (5 mol equiv.), the corresponding cycloadduct **2** of dimethylbutadiene was obtained (72%), along with anthracene. Similarly, the cyclopentadiene adduct **3** and dimethylbutadiene (6 mol equiv.) gave, when heated in toluene under reflux for 4 h, the cycloadduct **2** as the sole product after cyclopentadiene had been removed by evaporation of the solvent. Further, when the anthracene adduct **4** was heated under reflux in toluene for 1 h with cyclopentadiene (5.6 mol equiv.), the cyclopentadiene adduct **3** was the sole product (84%) apart from anthracene. Thus, as expected, interconversion of the cycloadducts **3** and **4** under these conditions favoured release of the aromatic 'diene', anthracene.

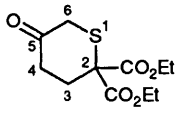
It was not possible to measure cycloaddition rates for the reactive intermediate **1**. Instead, the dissociation rate of the anthracene adduct **4** was measured, to provide an upper limit for the rate of preparative transfer of thioxomalonate **1** to other dienes, and a comparison with the dissociation rate of the corresponding thioxoacetate adduct **6**. The release of anthracene, monitored by UV absorption (λ_{max} 355 nm), from the cycloadducts **4** and **6** followed first-order kinetics in toluene at 100 °C in the presence of dimethylbutadiene (10 mol equiv.). This is consistent* with slow, rate-determining dissociation of the cycloadducts followed by rapid capture of the thioxo compounds by dimethylbutadiene. The half-lives of the thioxomalonate adduct **4** and the thioxoacetate adduct **6** were 35 and 109 min, respectively, at 100 °C. In practice, therefore, shorter reaction times or lower temperatures should suffice for preparative 'transfer' experiments with the thioketone **1** in comparison with those with ethyl thioxoacetate.

Ethyl thioxoacetate reacted with the 1-methoxycyclohexa-1,3-diene ring of the alkaloid thebaine to form almost exclusively one adduct regioisomer, with sulphur becoming bonded to C(4) of the diene.[1] The same mode of addition was shown by ethyl acrylate. It appeared therefore, at least from this one example, that the orientation of the thioaldehyde in Diels–Alder reactions was controlled largely by the electron-withdrawing carbonyl group. This conclusion is in accord with the wider theoretical and experimental findings of Vedejs *et al.*[6] For example, thioaldehydes **9** with electron-withdrawing groups (Z) react with 2-trimethylsiloxybuta-1,3-diene **8** to give predominantly the cycloadducts **10** (Scheme 2). Other thioaldehydes **11** react largely in the opposite sense **12**. The diene **8** was chosen to test the orientation of diethyl thioxomalonate **1** in Diels–Alder reactions. Thus, the



Scheme 2.

cycloadduct **4** was heated in toluene with the diene **8**, in the usual way. The ^1H and ^{13}C NMR spectra of the reaction mixture indicated the presence of only one cycloadduct, compound **13**, along with anthracene. The mixture was treated with aq. potassium fluoride, to cleave the trimethylsiloxy group, and the resulting ketone **14** was isolated and purified. The structure **14** could not be unambiguously distinguished from that of the 4-oxo isomer by spectroscopic data alone. Therefore, the ketone **14** was oxidised with peracetic acid to give the sulphoxide **15**. The ^{13}C NMR spectrum of compound **15** showed signals, δ 25.6, 37.1 and 57.6, from the ring-methylene carbons; the signal for C(6), adjacent to the sulphoxide group, was unambiguously identified by its large chemical shift, δ 57.6. The ^1H spectrum of compound **15** displayed an AB quartet, δ 3.64 and 4.09 (J_{gem} 14.5 Hz), for an isolated, ring-methylene group. A ^1H–^{13}C correlation experiment (COSY) then showed that this group was $C(6)H_2$, thus establishing the structures **15** and **14**. The AB quartet for $C(6)H_2$ showed fine splitting for one



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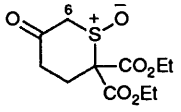

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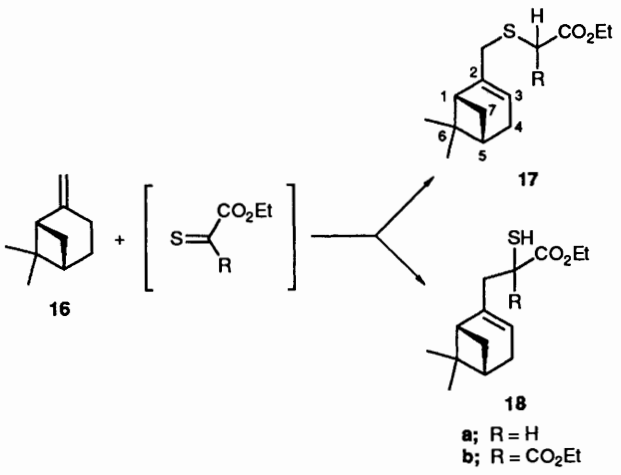
proton, δ 3.64 (dd, *J* 14.5 and 1.3 Hz). Presumably, this arises from 'W coupling' of the equatorial proton, and implies that the ring is locked in one conformation, on the NMR time-scale, by the sulphoxide oxygen. As expected, therefore, the thioketone **1**, with two attached ester groups, behaves like the thioaldehydes **9** in reactions with unsymmetrical dienes.

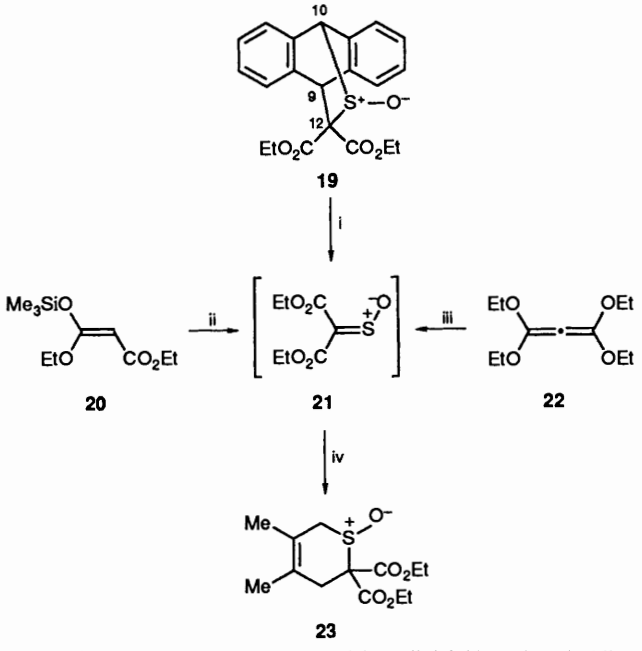
Ethyl thioxoacetate underwent an 'ene' reaction[1,7] with β-pinene **16** to give the products **17a** and **18a** in the ratio *ca.* 4:1 (Scheme 3). In contrast, when thiobenzaldehyde reacted with the same olefin,[8] the products of C–S (as **17**) and C–C (as **18**) bond formation were obtained in the ratio *ca.* 1:2. The anthracene adduct **4** was heated with an excess of β-pinene **16** in toluene under reflux for 1 h to afford the oily sulphide **17b** as the exclusive 'ene' product. The structure was revealed by signals at δ 3.25 (2 H, br s, SCH_2) and 4.11 [1 H, s, $CH(CO_2Et)_2$] in the ^1H NMR spectrum; the alternative product **18b** would have given a signal for a thiol proton, exchangeable with deuterium oxide. The same product was formed, as expected, when the cyclopentadiene adduct **3** was used as a thioxomalonate precursor. Again, it appears that the thioxomalonate **1** behaves in the 'ene' reaction like ethyl thioxoacetate, but its selectivity is enhanced by the second ester group.

* For a more detailed discussion of similar studies, with transient nitrosocarbonyl compounds, see G. W. Kirby and J. G. Sweeny, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3250. When heated *under reflux* in toluene for 10 min, the thioxomalonate adduct **4** and dimethylbutadiene (each 0.01 mol dm^{-3}) gave the dimethylbutadiene adduct **2** in *ca.* 50% yield (determined from the ^1H NMR spectrum of the reaction mixture), together with the unchanged precursor **4** and anthracene. The yield of the adduct **2** was not significantly increased when dimethylbutadiene was used in excess (0.10 mol dm^{-3}) for the same time and at the same temperature.



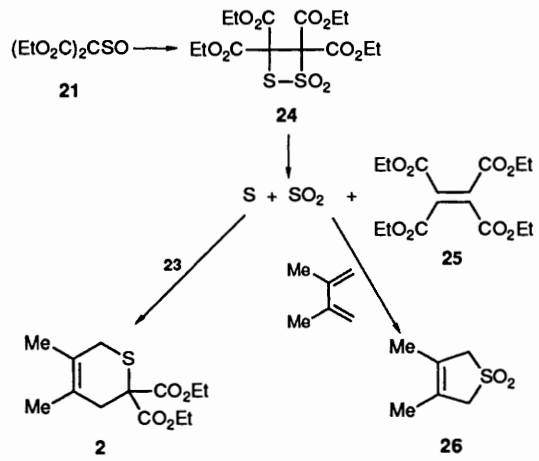
Scheme 3.

In 1985 two methods were reported,[9,10] independently, for the generation of the labile sulphine diethyl thioxomalonate oxide **21** (Scheme 4). The silyl enol ether **20** was cleaved at low



Scheme 4. *Co-reactants and conditions*: i, heat; ii, $SOCl_2$ and 2,6-lutidine; iii, $SOCl_2$; iv, 2,3-dimethylbuta-1,3-diene.

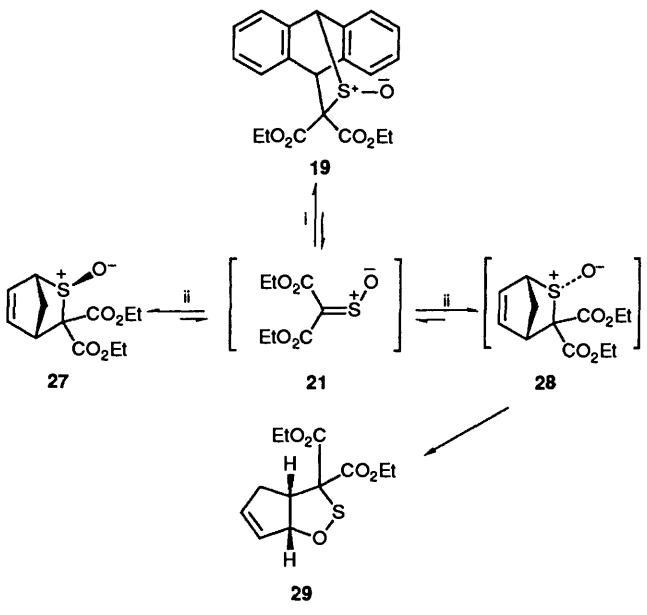
temperature with thionyl chloride in the presence of a base to give the sulphine **21**, which was trapped *in situ* with dimethylbutadiene (*ca.* 10 mol equiv.).[9] The cycloadduct **23** was obtained in 53% yield. Alternatively,[10] the allene **22** was cleaved with thionyl chloride at −78 °C, and dimethylbutadiene (5 mol equiv.) was added at −50 °C to trap the sulphine **21**. The major product **23** (42%) was accompanied by the corresponding sulphide **2**, tetraethyl ethenetetracarboxylate **25**, and the sulphone **26**. The by-products were believed to arise *via* the sulphine dimer **24** (Scheme 5), with sulphur dioxide being trapped by the butadiene, and sulphur, perhaps, reducing the sulphoxide **23**. Decomposition of the sulphine **21** in the absence of dimethylbutadiene gave the tetraester **25** as the sole identified product. We had shown[3] that the *Z* and *E* *S*-oxides of ethyl thioxoacetate could be generated cleanly from thermal cleavage of the corresponding *S*-oxides of the anthracene **6** and cyclopentadiene **7** cycloadducts. It seemed that the same



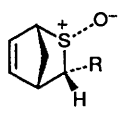
Scheme 5.

technique might be applied for the generation of the sulphine **21**. Importantly, slow and reversible release of the sulphine from a cycloadduct, in the presence of an appropriate co-reactant, should provide ideal conditions for the suppression of competitive formation of the dimer **24** and consequent by-products.

Accordingly, the anthracene cycloadduct **4** was treated with peracids, preferably peracetic acid in diethyl ether, to give the crystalline sulphoxide **19**. When this was heated in benzene (*ca.* 80 °C) under reflux for 1 h with dimethylbutadiene (5 mol equiv.), the cycloadduct **23** was obtained cleanly (64% after purification); none of the by-products shown in Scheme 5 was detected. A reference sample of the product **23** was prepared from the sulphide **2**. Similarly, peracid oxidation of the cyclopentadiene adduct **3** gave the *exo*-sulphoxide **27**, without any detectable amounts of the corresponding *endo*-isomer (**28**). The *exo* stereochemistry **27** was evident from the large chemical-shift difference, Δδ 0.69 ppm, for the NMR signals from the 7-methylene protons. A similar difference, Δδ 0.58 ppm, was observed[3] for the *exo*-sulphoxide of the *endo*-thioxoacetate adduct **7**, whereas a smaller value, Δδ 0.23 ppm, was observed for the sulphide **3**. Again, the cyclopentadiene adduct **27** and dimethylbutadiene (5 mol equiv.), in toluene at 111 °C for 1 h, gave the cycloadduct **23** (80%). However, a small quantity (*ca.* 5%) of the sultene **29** was detected (^{1}H NMR spectroscopy) in the reaction mixture (Scheme 6). This by-product was obtained in high yield when the cyclopentadiene adduct **27** was heated alone in toluene. It must arise from the *endo*-sulphoxide **28** formed by dissociation of the *exo*-isomer **27** followed by recombination of the components in the opposite sense. [2,3]-Sigmatropic rearrangements of the type **28** ⟶ **29** were first discovered by Block and Wall[11] for cyclopentadiene adducts **30** of thioaldehyde (*Z*)-sulphines; the corresponding *exo*-sulphoxides were thermally stable. When the anthracene adduct **19** was heated with cyclopentadiene in benzene (80 °C) for 1 h, a 2:1 mixture of the *exo*-sulphoxide **27** and the sultene **29** was obtained. A control experiment showed that the sulphoxide **27** was stable under these conditions. As expected, when the anthracene adduct **19** was heated with cyclopentadiene in toluene (111 °C) the sultene **29** was obtained as the sole product, apart from anthracene. The 2:1 ratio of the products **27** and **29** formed at 80 °C does not necessarily reflect the *exo*:*endo* ratio of cycloaddition of the sulphine **21** to cyclopentadiene. In principle, the putative intermediate **28** might isomerise, by dissociation and recombination, into the *exo*-sulphoxide, which is stable at this temperature, at a rate comparable with that of the sigmatropic rearrangement to give the sultene **29**. To clarify this point, the sulphine was generated by flash vacuum pyrolysis (FVP) and its reactivity was studied at low temperature.



Scheme 6. *Co-reactants*: i, anthracene; ii, cyclopentadiene.



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The anthracene adduct **19** was sublimed (160 °C; *ca.* 10^{-4} mbar*) through a silica tube at 500 °C. Anthracene condensed on the cool wall of the tube outside the furnace and the more volatile products were collected in a trap cooled in liquid nitrogen. Cyclopentadiene was added to the trap, which was then allowed to warm up to room temperature. Examination of the resulting mixture by ^{1}H NMR spectroscopy showed the presence of the *exo*-sulphoxide **27**, traces of diethyl malonate, and unidentified material derived from the sulphine **21**. Some sulphur was detected by TLC. No signals attributable to either the *endo*-sulphoxide **28** or the sultene **29** were observed. The major component **27** was isolated by chromatography (47%). When the volatile products were collected in the cold-trap in the absence of cyclopentadiene, and allowed to warm to room temperature, a mixture was obtained containing some diethyl malonate and sulphur and, again, ill defined products from the sulphine. None of the tetraester **25** was detected. The diethyl malonate is believed to arise from hydrolysis[12] of the sulphine **21** by traces of water in the apparatus. Thus, when the sulphine **21** was collected in a cold-trap containing water (ice), the resulting product mixture consisted largely of diethyl malonate together with sulphur and, once more, some ill defined material. The last product must arise by polymerisation of the sulphine. The ^{1}H NMR spectrum showed only broad signals for ethoxycarbonyl groups, and the mass spectrum contained no peaks attributable to the molecular ion of the sulphine **21** or of its dimer or higher polymers. Hydrolysis of the sulphine presumably involves nucleophilic addition of water to sulphur and protonation on carbon, followed by loss of sulphur dioxide, or sulphurous acid. Thiophilic attack by nucleophiles on sulphines having electron-withdrawing substituents has been observed before.[12] Clearly, the sulphine **21** survives the conditions of FVP, as does the parent sulphine, thioformaldehyde *S*-oxide.[13] However, the observation that, at least at low temperatures, it adds to cyclopentadiene largely or entirely to give the *exo*-adduct **27** was surprising. Thioformaldehyde *S*-oxide and various *cis*-alkyl sulphines all add preferentially to form the *endo*-sulphoxides (**30**; R = H or alkyl).[11] Perhaps the ester group in compound **21** *cis* to the sulphoxide oxygen is twisted out of the CSO plane, whereas the *trans*-ester carbonyl group is coplanar with the sulphine group and can assist cycloaddition by the usual *endo* effect. The absence of the tetraester **25** in the decomposition products of the sulphine, trapped at low temperature, was also unexpected. However, in the condensed phase, polymerisation may be favoured over formation of the dimer **24**, which must involve more than one step.

As with the thioketone **1**, it was not possible to measure the rates of cycloaddition of the sulphine **21** or to compare them with those of the related thioaldehyde sulphines, ethyl thioxoacetate (*Z*)- and (*E*)-*S*-oxide. However, a competition experiment was carried out to check whether the sulphine **21**, like common dienophiles, reacted faster with cyclopentadiene than with dimethylbutadiene. Indeed, the anthracene adduct **19** with cyclopentadiene (3 mol equiv.) and dimethylbutadiene (3 mol equiv.) at 80 °C in benzene for 1 h gave, as before, a mixture of the cyclopentadiene derivatives **27** and **29** (2:1) containing none of the cycloadduct **23**. Finally, the dissociation rate of the anthracene adduct **19** was measured for comparison with that of the *trans*-sulphoxide of the thioaldehyde adduct (**6**; R = Me). The release of anthracene from the cycloadduct **19** was monitored (λ_{max} 355 nm) in benzene at 60 °C in the presence of dimethylbutadiene (10 mol equiv.). The half-life of the adduct, 41 min, was approximately half that measured for the *trans*-sulphoxide of the adduct (**6**; R = Me), $t_{\frac{1}{2}}$ 76 min at 60 °C. The high dissociation rate of the thioxomalonate oxide cycloadduct **19** emphasises its potential as a preparative source of the sulphine **21** under mild conditions. The cyclopentadiene adduct **27** is useful too, despite its lower dissociation rate, because the liberated cyclopentadiene is highly volatile. However, with co-reactants less reactive than dimethylbutadiene, competitive isomerisation to give the sultene **29** will seriously interfere.

Experimental

General Methods.—NMR spectra were recorded for deuteriochloroform solutions, and mass spectra were obtained by electron impact at 70 eV. TLC was carried out on Merck silica gel 60 G_{254} plates and compounds were located by UV light or iodine vapour. Extracts in organic solvents were dried over $MgSO_4$ and evaporated in a Buchi Rotavapor. Light petroleum refers throughout to the fraction boiling in the range 40–60 °C.

Diethyl 2-Thiabicyclo[2.2.1]*hept-5-ene-3,3-dicarboxylate* **3**.—A solution of diethyl oxomalonate (2.01 g, 11.6 mmol) in dry pyridine (25 cm^3) was added dropwise during 10 min to a mixture of phosphorus pentasulphide (0.98 g, 4.41 mmol) and cyclopentadiene (3.71 g, 56.2 mmol) in dry pyridine (100 cm^3) under reflux under nitrogen. After 1 h the mixture was cooled to room temperature and then acidified with dil. hydrochloric acid. The mixture was extracted with diethyl ether, and the extracts were washed successively with dil. hydrochloric acid, aq. sodium hydrogen carbonate and water, and were dried and evaporated. The residual, yellow oil (3.63 g) was distilled to give the *cycloadduct* **3** (1.76 g, 60%), b.p. 106 °C (0.08 mmHg) (Found: C, 55.95; H, 6.45; S, 12.8%; M^+, 256.0770. $C_{12}H_{16}O_4S$ requires C, 56.2; H, 6.3; S, 12.5%; M, 256.0769); ν_{max}(liquid film): 1755sh and 1740 cm^{-1}; δ_H(200 MHz): 1.23 (t, *J* 7.1 Hz, Me), 1.24 (t, *J* 6.7 Hz, Me), 1.79 (dt, *J* 9.6 and 2.2 Hz, 7-H), 2.02 (dm, *J* 9.6 Hz, 7-H), 3.85 and 4.10 (2 m, 1- and 4-H), 4.09–4.34 (m, 2 × OCH_2), 5.84 (dd, *J* 5.5 and 3.1 Hz, 5- or 6-H) and 6.52 (dd, *J* 5.5 and 2.9

* 1 bar = 10^5 Pa.

Hz, 6- and 5-H); δ_C(50.3 MHz): 13.9 and 14.0 (2 × Me), 51.4 (C-7), 52.5 and 52.8 (C-1 and -4), 62.1 (2 × OCH_2), 68.9 (C-3), 131.3 and 140.2 (C-5 and -6) and 168.8 and 170.2 (2 × C=O).

Alternatively,[4] a solution of diethyl dibromomalonate (0.52 g, 1.63 mmol) in acetone (10 cm^3) was added dropwise during 10 min to a stirred mixture of potassium *O*-ethyl xanthate (0.65 g, 4.06 mmol) and cyclopentadiene (2.02 g, 30.6 mmol) in acetone (15 cm^3) cooled in ice. After 2 h, the mixture was allowed to warm up to room temperature overnight and was then filtered. The filtrate was evaporated to give a brown residue, which was separated by TLC in diethyl ether–light petroleum (3:7) to afford the cycloadduct **3** (310 mg, 74%), having a ^1H NMR spectrum identical with that of the foregoing material.

Diethyl 3,6-*Dihydro*-4,5-*dimethyl*-2H-*thiine*-2,2-*dicarboxylate* **2**.—Diethyl oxomalonate was treated with phosphorus pentasulphide in dry pyridine in the presence of an excess of 2,3-dimethylbuta-1,3-diene under reflux under nitrogen, in the manner described above for the preparation of the cyclopentadiene adduct **3**. The product was distilled to give the cycloadduct **2**[4] (56%), b.p. 112 °C (0.2 mmHg) (Found: C, 57.35; H, 7.8; S, 12.1%; M^+, 272.1074. Calc. for $C_{13}H_{20}O_4S$: C, 57.3; H, 7.4; S, 11.7%; M, 272.1082); ν_{max}(liquid film): 1735 cm^{-1}; δ_H(90 MHz): 1.23 (t, *J* 7 Hz, 2 × OCH_2*Me*), 1.70 (br s, 4- and 5-Me), 2.67 (br s, 3-H_2), 3.06 (br s, 6-H_2) and 4.22 (q, *J* 7 Hz, 2 × OCH_2); δ_C(50.3 MHz): 13.9 (2 × OCH_2*Me*), 19.1 and 20.0 (4- and 5-Me), 30.9 (C-3), 37.7 (C-6), 56.7 (C-2), 62.2 (2 × OCH_2), 122.9 and 125.4 (C-4 and -5) and 168.8 (2 × C=O). The ^1H NMR spectrum was identical with that of a sample prepared[4] using potassium *O*-ethyl xanthate, as described above for the cycloadduct **3**.

Diethyl 9,10-*Dihydro*-10,9-(*epithiomethano*)*anthracene*-12,12-*dicarboxylate* **4** (*with M. C. McGuire*).—A solution of diethyl oxomalonate (1.25 g, 7.18 mmol) in dry pyridine (10 cm^3) was added dropwise during 10 min to a stirred mixture of phosphorus pentasulphide (0.72 g, 3.24 mmol) and anthracene (6.30 g, 35.4 mmol) in dry pyridine (90 cm^3) at 70–80 °C under nitrogen. The mixture was heated for a further 1 h, cooled, and was acidified with dil. hydrochloric acid. The mixture was extracted with diethyl ether and the extracts were filtered to remove any anthracene that had separated out. The filtrate was washed successively with dil. hydrochloric acid, aq. sodium hydrogen carbonate and water and was dried and evaporated. The residue was kept under reduced pressure over phosphorus pentaoxide to remove traces of pyridine. The residual solid (5.48 g) was shaken with methanol (2 × 50 cm^3) and the methanolic extracts were filtered to remove anthracene. The filtrate was evaporated and the residue (1.93 g) was treated with boiling methanol (30 cm^3) and filtered. The filtrate was kept at *ca.* 5 °C overnight to allow crystallisation of the product. The crystals were collected, and washed with light petroleum (2 × 10 cm^3), to afford the *cycloadduct* **4** (617 mg, 23%) as shiny white plates, m.p. 150–152 °C (Found: C, 68.35; H, 5.4; S, 8.9%; M^+, 368.1075. $C_{21}H_{20}O_4S$ requires C, 68.5; H, 5.5; S, 8.7%; M, 368.1082); ν_{max}(KBr): 1745 cm^{-1}; δ_H(200 MHz): 1.16 (t, *J* 7.1 Hz, 2 × Me), 4.06 and 4.10 (q ABq, *J* 7.2 and 10.8 Hz, 2 × OCH_2), 5.14 (s, 9- or 10-H), 5.34 (s, 10- or 9-H) and 7.1–7.5 (m, ArH); δ_C(50.3 MHz): 13.8 (2 × Me), 46.7 and 50.7 (C-9 and C-10), 62.3 (2 × OCH_2), 68.6 (C-12), 122.0, 125.3, 126.0 and 126.1 (ArCH), 138.8 and 143.1 (ArC) and 168.2 (2 × C=O).

A solution of the diester **4** in THF was heated with an excess of aq. ethanolic sodium hydroxide under reflux. Work-up in the usual way gave the monocarboxylic acid **5**, m.p. 178–181 °C (from Et_2O), which gave a ^1H NMR spectrum identical with that of a sample prepared from the ester **6**.[1]

Preparation of the Cyclopentadiene Adduct **3** *from the Bunte Salt Derived from Diethyl Bromomalonate* (*with G. El Naggar*).—Diethyl bromomalonate was heated in ethanol with an equimolecular amount of disodium thiosulphate pentahydrate, in the usual way,[14] to form the corresponding sodium thiosulphate *S*-ester (Bunte salt). This salt, without purification, was treated at room temperature for 24 h in ethanol with equimolecular amounts of cyclopentadiene, calcium chloride dihydrate and triethylamine, in the usual way.[2] Preparative TLC (PLC) of the organic products gave the cycloadduct **3** (52%), the *endo*-ester **7** (17%) and the *exo*-ester **7** (6%). The products were identified by comparison of their ^1H NMR spectra with those of reference samples.[2]

Retro-Diels–Alder Reactions of the Cycloadducts **3** *and* **4** *with Dimethylbutadiene and Cyclopentadiene*.—The anthracene adduct **4** (150 mg, 0.41 mmol) and 2,3-dimethylbuta-1,3-diene (169 mg, 2.06 mmol) were heated under reflux in dry toluene (30 cm^3) under nitrogen for 1 h. The mixture was evaporated and the products were separated by TLC in dichloromethane–light petroleum to give the dimethylbutadiene adduct **2** (79.2 mg, 71%) and anthracene. Similarly, the cycloadduct **4** (0.23 mmol) and cyclopentadiene (1.28 mmol) were heated in toluene (20 cm^3) for 1 h to give, after TLC, the cyclopentadiene adduct **3** (0.193 mmol, 84%). The cyclopentadiene adduct **3** (0.41 mmol) and dimethylbutadiene (2.6 mmol) were heated, as before, in toluene for 4 h to give directly, afer evaporation of the mixture, the oily dimethylbutadiene adduct **2** (0.40 mmol, 98%) without any significant by-products as judged by ^1H NMR spectroscopy.

Dissociation Rates of the Cycloadducts **4** *and* **6**.—Each cycloadduct **4** and **6** (0.040 mmol) was dissolved separately in dry toluene (50 cm^3) containing 2,3-dimethylbuta-1,3-diene (0.40 mmol). Aliquots (2 cm^3), sealed under nitrogen in separate tubes, were heated in a water-bath at 100 ± 1 °C. Tubes were removed after various time intervals and cooled immediately in ice–water. The contents of each tube were diluted with hexane (final volume 10 cm^3) for UV assay of anthracene (λ 355 nm). The release of anthracene followed first-order kinetics with $t_{\frac{1}{2}}$ 35 and 109 min for the cycloadducts **4** and **6**, respectively.

Diethyl 5-*Oxothiane*-2,2-*dicarboxylate* **14** *and the Corresponding* S-*Oxide* **15**.—The anthracene adduct **4** (144 mg, 0.39 mmol) and 2-(trimethylsiloxy)buta-1,3-diene **8** (0.10 cm^3, 1.0 mmol) were heated under reflux in dry toluene under nitrogen for 1 h. The mixture was evaporated and the residue was found by NMR spectroscopy to contain anthracene, a small amount of the oxothiane **14**, and the cycloadduct **13**; δ_H(200 MHz): 0.17 (s, Me_3Si), 1.27 (t, *J* 7.0 Hz, 2 × OCH_2*Me*), 2.89 (dt, *J* 4.5 and 2.2 Hz, 3-H_2), 3.12 (d, *J* 1.4 Hz, 6-H_2), 4.22 (q, *J* 7.0 Hz, 2 × OCH_2) and 4.95 (t, *J* 4.5 Hz, with fine splitting, 4-H); δ_C(50.3 Hz): 1.85 (Me_3Si), 13.9 (2 × OCH_2*Me*), 28.3 (C-3 or -6), 32.3 (C-6 or -3), 55.4 (C-2), 62.3 (2 × OCH_2), 102.8 (C-4), 146.1 (C-5) and 168.2 (2 × C=O).

The crude product was treated with potassium fluoride (58 mg) in THF (10 cm^3) containing water (*ca.* 200 mg) for 24 h at room temperature. The mixture was evaporated and the residue was extracted with dichloromethane. The extracts were washed with water, then dried and evaporated. The residue was extracted with methanol and the extract was filtered to remove anthracene. Evaporation of the filtrate and chromatography of the residue on silica plates developed with dichloromethane–light petroleum (2:3) gave the *oxothiane* **14** (52 mg, 51%) as a yellow oil (Found: M^+, 260.0711. $C_{11}H_{16}O_5S$ requires M, 260.0719); ν_{max}(liquid film): 1730 cm^{-1}; δ_H(200 MHz): 1.24 (t, *J* 7.1 Hz, 2 × Me), 2.60 and 2.71 (2 m, 3- and 4-H_2), 3.30 (s, 6-H_2) and 4.24 (q, *J* 7.1 Hz, 2 × OCH_2); δ_C(50.3 MHz): 13.9

(2 × Me), 33.2, 35.7 and 36.4 (ring CH_2), 56.0 (C-2), 62.7 (2 × OCH_2), 168.4 (2 × CO_2) and 203.0 (C-5).

A solution of the oxothiane **14** (68 mg, 0.25 mmol) in diethyl ether (30 cm^3) was treated dropwise during 10 min with peracetic acid (27% w/w in acetic acid; 0.30 mmol) in diethyl ether (5 cm^3) at room temperature. After a further 1 h the solution was evaporated and the residue was dissolved in dichloromethane (50 cm^3). The solution was washed successively with aq. sodium hydrogen carbonate and water and then was dried and evaporated to give the *S*-oxide **15** as an oil (54 mg, 78%); δ_H(200 MHz): 1.29 and 1.31 (2 t, *J* 7.1 Hz, 2 × Me), 2.54 (m, 3- or 4-H_2), 2.75 (dt, *J* 15.1 and 4.5 Hz, 4- or 3-H), 3.13 (ddd, *J* 15.1, 11.4 and 6.0 Hz, 4- or 3-H), 3.64 (dd, *J* 14.5 and 1.3 Hz, 6-H), 4.09 (d, *J* 14.4 Hz, 6-H) and 4.23–4.42 (m, 2 × OCH_2); δ_C(50.3 MHz): 13.9 (2 × Me), 25.6 (C-3), 37.1 (C-4), 57.6 (C-6), 63.4 and 63.6 (2 × OCH_2), 71.3 (C-2), 164.2 and 165.9 (2 × CO_2) and 198.7 (C-5). A ^1H–^{13}C, one-bond, correlation experiment (COSY) showed, *inter alia*, clear correlation between the signal at δ_C 57.6 and the signals at δ_H 3.64 and 4.09.

'Ene' Reaction of the Thioxomalonate **1** *with* β-*Pinene*.—The anthracene adduct **4** (260 mg, 0.71 mmol) and (−)-β-pinene **16** (250 mg, 1.8 mmol) were heated under reflux in dry toluene under nitrogen for 1 h. The mixture was evaporated and the residue separated by TLC with dichloromethane–light petroleum (1:1) to give the *pinyl sulphide* **17b** as an oil (140 mg, 60%) (Found: C, 62.3; H, 7.9; S, 10.0%; M^+, 326.1571. $C_{17}H_{26}O_4S$ requires C, 62.55; H, 8.0; S, 9.9%; M, 326.1552); $[\alpha]_D^{22}$ −8° (in MeOH); ν_{max}(liquid film): 1745sh and 1730 cm^{-1}; δ_H(90 MHz): 0.80 and 1.26 (2 s, 6-Me_2), 1.26 (t, *J* 7 Hz, 2 × OCH_2*Me*), 2.0–2.5 (m, 1- and 5-H and 4- and 7-H_2), 3.25 (br s, SCH_2), 4.11 [s, SC*H*$(CO_2Et)_2$], 4.22 (q, *J* 7 Hz, 2 × OCH_2) and 5.47 (br s, 3-H). The same product **17b** was obtained when the cyclopentadiene adduct **3** was heated under the same conditions with β-pinene but for a longer period (4 h).

The Cycloadduct **19** *of Anthracene and the Sulphine* **21**.—A solution of peracetic acid (27% w/w in acetic acid; 0.75 mmol) in diethyl ether (5 cm^3) was added dropwise during 10 min to a stirred solution of the anthracene adduct **4** (270 mg, 0.73 mmol) in diethyl ether (30 cm^3) at room temperature. After 1 h, the solution was evaporated and the residue was dissolved in dichloromethane (50 cm^3). This solution was washed successively with aq. sodium hydrogen carbonate and water, and was then dried and evaporated. Crystallisation of the residue from methanol or diethyl ether gave diethyl 9,10-dihydro-10,9-(epithiomethano)anthracene-12,12-dicarboxylate S-oxide **19** as white plates (336 mg, 79%), m.p. 94–98 °C; ν_{max}(KBr): 1735 cm^{-1}; δ_H(200 MHz): 1.10 and 1.20 (2 t, *J* 7.0 Hz, 2 × Me), 3.91–4.36 (m, 2 × OCH_2), 5.26 and 5.78 (2 s, 9- and 10-H), and 7.21–7.56 (m, Ar H); δ_C(50.3 MHz): 13.9 (2 × Me), 49.7 (C-9), 62.5 (2 × OCH_2), 68.1 (C-10), 82.7 (C-12), 125.5, 127.3, 127.4, 127.8, 128.1, 128.35 and 128.8 (ArCH), 132.9, 136.0 and 138.6 (ArC) and 162.9 and 165.8 (2 × C=O). This compound gave inconsistent elemental analyses; as expected, the mass spectrum showed a base peak, *m/z* 178, corresponding to anthracene and no molecular-ion peak. The same sulphoxide **19** was obtained also, sometimes in high yield, from the cycloadduct **4** and 3-chloroperbenzoic acid in dichloromethane, but the yields were inconsistent.

Diethyl 3,6-*Dihydro*-4,5-*dimethyl*-2H-*thiine*-2,2-*dicarboxylate* S-*Oxide* **23**.[9,10]—The anthracene cycloadduct **19** (68 mg, 0.18 mmol) and 2,3-dimethylbuta-1,3-diene (73 mg, 0.89 mmol) were heated under reflux in dry benzene (15 cm^3) under nitrogen for 1 h. The mixture was evaporated and the residue was separated by TLC in diethyl ether to give the sulphoxide **23** as an oil (32 mg, 62%), b.p. 140 °C (0.1 mmHg) (measured on a larger sample, see below) (Found: C, 54.1; H, 6.8; S, 11.4%; M^+, 288.1032. Calc. for $C_{13}H_{20}O_5S$; C, 54.15; H, 7.0; S, 11.1%; M, 288.1032); ν_{max}(liquid film): 1750sh and 1730 cm^{-1}; δ_H(90 MHz) 1.13 and 1.16 (2 t, *J* 7 Hz, 2 × OCH_2*Me*), 1.56 and 1.64 (s, 4- and 5-Me), 2.57 and 2.92 (br ABq, 3- or 6-H_2), 3.10 and 3.42 (br ABq, 6- or 3-H_2), and 4.09 and 4.19 (2 m, 2 × OCH_2); δ_C(50.3 MHz): 13.5 (2 × OCH_2*Me*), 18.8 and 19.9 (4- and 5-Me), 27.7 (C-3), 50.8 (C-6), 62.2 and 62.5 (2 × OCH_2), 70.0 (C-2), 115.9 and 124.9 (C-4 and -5), and 184.9 and 185.3 (2 × C=O). This sulphoxide **23** was also obtained from the sulphide **2** by oxidation with 3-chloroperbenzoic acid in dichloromethane, as described below for the cyclopentadiene adduct **3**.

Diethyl 2-*Thiabicyclo*[2.2.1]*hept*-5-*ene*-3,3-*dicarboxylate* exo-S-*Oxide* **27**.—A solution of 3-chloroperbenzoic acid (0.94 g, 5.47 mmol) in dichloromethane (10 cm^3) was added dropwise during 15 min to a shaken solution of the cycloadduct **3** (1.29 g, 5.04 mmol) in dichloromethane (10 cm^3) at room temperature. After 1 h, the mixture was diluted with dichloromethane (30 cm^3), washed successively with 10% aq. sodium sulphite (2 × 30 cm^3) and water, and then dried and evaporated. The *sulphoxide* **27** was obtained as an undistillable yellow oil (1.21 g, 88%), which was purified by TLC in dichloromethane (Found: C, 52.7; H, 6.2; S, 11.8%. M^+, 272.0715. $C_{12}H_{16}O_5S$ requires C, 52.9; H, 5.9; S, 11.8%; M, 272.0719); ν_{max}(liquid film): 1735 cm^{-1}; δ_H(90 MHz) 1.20 (t, *J* 7 Hz, 2 × Me), 2.35 (dt, *J* 12 and 2 Hz, 7-H), 3.04 (d, *J* 12 Hz, 7-H), 3.62 (br s, 1- or 4-H), 4.0–4.3 (m, 4- or 1-H, and 2 × OCH_2) and 6.00 and 6.14 (2 dd, *J* 6 and 3 Hz, 5- and 6-H); δ_C(50.3 MHz): 13.9 and 14.0 (2 × Me), 45.7 (C-7), 47.8 (C-4), 62.3 and 62.7 (2 × OCH_2), 69.0 (C-1), 83.0 (C-3), 130.2 and 141.1 (C-5 and -6) and 164.0 and 166.0 (2 × C=O).

Retro-Diels–Alder Reactions of the Cyclopentadiene Sulphine Adduct **27**; *Formation of the Sultene* **29**.—The cycloadduct **27** (120 mg, 0.44 mmol) and 2,3-dimethylbuta-1,3-diene (183 mg, 2.23 mmol) were heated under reflux in dry toluene (20 cm^3) under nitrogen for 1 h. The mixture was evaporated. The ^1H NMR spectrum of the residual oil (127 mg) showed it to contain the dimethylbutadiene adduct **23** and the sultene **29** (*ca.* 5%). TLC in diethyl ether gave the cycloadduct **23** (102 mg, 80%).

The cycloadduct **27** (3.10 g, 11.4 mmol) was then heated alone, under the foregoing conditions, for 1 h to give *diethyl* cis-2-*oxa*-3-*thiabicyclo*[3.3.0]*oct*-7-*ene*-4,4-*dicarboxylate* **29** (2.72 g, 88%) as an oil that decomposed upon attempted distillation or PLC (Found: M^+, 272.0724. $C_{12}H_{16}O_5S$ requires M, 272.0718); ν_{max}(liquid film) 1790 and 1735 cm^{-1}; δ_H(200 MHz): 1.24 (t, *J* 7.0 Hz, Me), 1.25 (t, *J* 7.2 Hz, Me), 2.19 (ddq, *J* 17.8, 4.6 and 2.3 Hz, 6-H), 2.56 (ddt, *J* 17.8, 8.6 and 2.2 Hz, 6-H), 3.63 (ddd, *J* 8.5, 6.3 and 4.5 Hz, 5-H), 4.21 and 4.23 (2 m, 2 × OCH_2), 5.54 (dt, *J* 6.3 and 2.2 Hz, 1-H), 5.68 (dq, *J* 5.9 and 2.3 Hz, 7- or 8-H) and 6.10 (dt, *J* 5.9 and 2.2 Hz, 8- or 7-H): δ_C(25.1 MHz): 14.0 (2 × Me), 36.1 (C-6), 48.7 (C-5), 62.5 (2 × OCH_2), 76.0 (C-4), 97.6 (C-1), 128.2 (C-7 or -8), 138.2 (C-8 or -7) and 166.0 and 168.8 (2 × C=O).

This sultene **29** was also obtained (71%) from the anthracene adduct **19** and cyclopentadiene (5 mol equiv.) under the foregoing conditions.

Concurrent Formation of the Cyclopentadiene Adduct **27** of the Sulphine **21** *and the Corresponding Sultene* **29**.—The anthracene adduct (31 mg, 0.081 mmol) and cyclopentadiene (27 mg, 0.41 mmol) were heated under reflux in dry benzene (5 cm^3) under nitrogen until the reaction was judged (TLC) to be complete (40 min). The ^1H NMR spectrum of the reaction mixture showed the presence of the sulphoxide **27** and the sultene **29** (2:1), and anthracene. The sulphoxide **27** was unchanged when heated alone under these conditions.

Flash Vacuum Pyrolysis (FVP) *of the Anthracene Sulphine Cycloadduct* **19**.—A solution of the cycloadduct **19** (122 mg, 0.32 mmol) in dichloromethane was stirred with finely ground, anhydrous magnesium sulphate (0.63 g). The mixture was evaporated and the resulting powder was kept under vacuum over P_2O_5 to remove any traces of solvent. The powder was heated (Buchi Kugelrohr oven) at *ca.* 160 °C and the cycloadduct **19** was allowed to sublime through a horizontal silica tube (2.5 × 50 cm) at 500 °C and 3×10^{-4} mbar during *ca.* 10 min. Anthracene crystallised in the cool section of the tube outside the furnace, and the more volatile products were condensed in a U-tube, cooled in liquid nitrogen, containing cyclopentadiene (212 mg, 3.2 mmol). The apparatus was then filled with nitrogen at atmospheric pressure and a solution of cyclopentadiene (208 mg, 3.2 mmol) in dichloromethane (10 cm^3) was added to the U-tube. The contents of the U-tube were allowed to warm up to room temperature and then were evaporated. The residual oil (57 mg) was examined by ^1H NMR spectroscopy, which showed that *ca.* 70% of the trapped sulphine **21** had formed the *exo*-sulphoxide **27**; the remainder was represented by ill defined material together with a trace of diethyl malonate. A small amount of sulphur was detected ($AgNO_3$ spray) by TLC. PLC gave the *exo*-sulphoxide **27** (41 mg, 47%).

In a similar experiment, the sulphine **21** was condensed in a U-tube, cooled in liquid nitrogen, containing water (*ca.* 20 mol equiv.). The contents of the U-tube were isolated as before and found to contain diethyl malonate (representing *ca.* 60% of the trapped sulphine), identified by ^1H and ^{13}C NMR spectroscopy. The other 40% appeared to be the same (^1H NMR) as the ill defined material from the first experiment. Sulphur was again detected by TLC. The 'ill defined material' was the major product, apart from anthracene, isolated when the sulphine was trapped in the absence of cyclopentadiene or water. The mass spectrum did not show peaks corresponding to the dimer ($C_{14}H_{20}O_{10}S_2$) or higher oligomers of the sulphine **21**. The major peaks of high mass were observed at *m/z* 382.0751 ($C_{14}H_{22}O_8S_2$ requires M, 382.0805), 380.0604 ($C_{14}H_{20}O_8S_2$, 380.0557), 368.1134 ($C_{14}H_{24}O_9S$, 368.1205) and 350.1045 ($C_{14}H_{22}O_8S$, 350.0945).

Dissociation Rate of the Cycloadduct **19**.—The procedure described above for the cycloadducts **4** and **6** was used for the sulphoxide **19**, except that aliquot samples were maintained at 60 ± 1 °C in a water-bath. The release of anthracene from adduct **19** in benzene at 60 °C showed $t_{\frac{1}{2}}$ 41 min.

Acknowledgements

We thank Miss M. C. McGuire and Professor G. El Nagaar for the experiments indicated, Professor J. K. Sutherland for helpful discussions and the J. D. Loudon Bequest and the SERC for financial support.

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Paper 0/02701D
Received 15*th June* 1990
Accepted 23*rd July* 1990