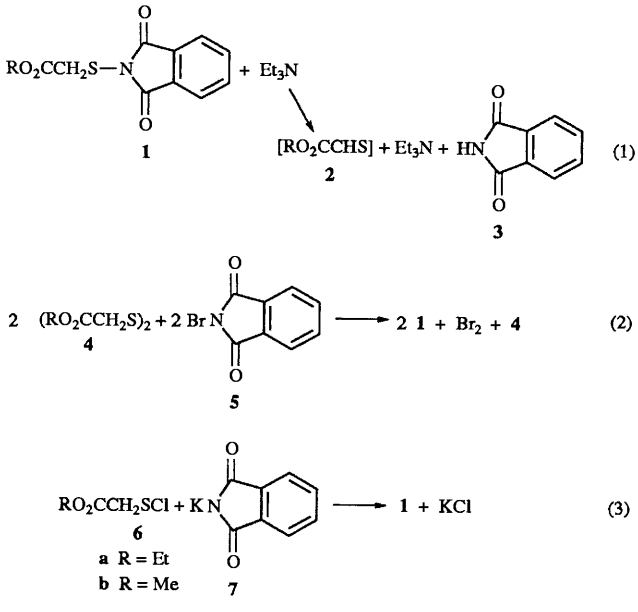
Dienophilic thioaldehydes and dithioesters formed by base-catalysed cleavage of alkyl phthalimidosulfanylacetates

Gordon W. Kirby,* Alistair W. Lochead and Sharon Williamson

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

Treatment of ethyl and methyl phthalimidosulfanylacetate 1a and 1b with triethylamine at room temperature generates [eqn. (1)] the transient thioaldehydes, ethyl and methyl thioxoacetate 2, which have been trapped *in situ* with 2,3-dimethylbuta-1,3-diene to yield the Diels–Alder cycloadducts 8a and 8b in high yield. The cycloadducts 9, 10 and 11a and 12a of ethyl thioxoacetate 2a and anthracene, cyclohexa-1,3-diene and cyclopentadiene, respectively, were obtained similarly. The *endo*-11a and *exo*-12a cycloadducts of cyclopentadiene, formed in the ratio *endo*:*exo* = 7:3, dissociate reversibly when heated in toluene under reflux, to give the same, equilibrium mixture, *endo*:*exo* = 3:7, and thereby can serve as 'clean' auxiliary precursors of ethyl thioxoacetate 2a. Thus, when mixtures of the cycloadducts 11a and 12a were heated in turn with dimethylbutadiene and (*E*,*E*)-1,4-diphenylbuta-1,3-diene, the corresponding cycloadducts 8a and 13 of the dienes were obtained. Unexpectedly, treatment of the thioxoacetate precursor 1a with triethylamine (1 mol equiv.) and 4-dimethylaminopyridine (DMAP) (0.1 mol equiv.) in the presence of dimethylbutadiene gave the thioxoacetate adduct 8a and, as the major product, the cycloadduct 15a of the dithioester 16. In the presence of cyclopentadiene, relatively less of the corresponding dithioester adducts 17 was formed, but the amount increased when DMAP alone was used to effect elimination. The dienophilic dithioester 16, formed from the precursor 1a and DMAP in the absence of any diene, was isolated and used to prepare the cycloadducts 15a, 17 and 19 in good yield. The cyclopentadiene adducts 17, like those of ethyl thioxoacetate, dissociated thermally and can serve as auxiliary precursors of the dithioester 16, *e.g.* in the preparation of the dimethylbutadiene adduct 15a.

We have reported[1] new routes to transient, dienophilic thioaldehydes, ZCHS, involving base-mediated, 1,2-elimination of HX from sulfenyl derivatives, ZCH_2SX, where Z is usually an electron-withdrawing group able to enhance both the rate of elimination and the dienophilic character of the thioaldehydes. Generally, the labile thioaldehydes were trapped *in situ* by cycloaddition to conjugated dienes to form dihydrothiines (dihydrothiopyrans). Initial experiments employed alkoxycarbonylmethanesulfenyl chlorides **6**, which reacted rapidly at room temperature with triethylamine to form the corresponding alkyl thioxoacetates **2**. When the sulfenyl chlorides were added to mixtures of various conjugated dienes and triethylamine, cycloadducts of the thioxoacetates and the dienes were obtained in satisfactory yield. However, by-products often arose from direct attack of the sulfenyl chlorides on the dienes in competition with elimination to give the thioaldehydes. We therefore sought sulfenyl derivatives which would not react significantly with conjugated dienes yet would still undergo 1,2-elimination at preparatively useful rates. In fact, the derivatives ZCH_2SX having X = N-phthaloyl,[2] SO_3Na (Bunte salts)[3] or *p*-$MeC_6H_4SO_2$[4] met these criteria. Here, we describe the preparation of the *N*-phthaloylsulfenamides **1** and their use as thioaldehyde[2] **2** [eqn. (1)] and dienophilic dithioester, *e.g.* **16**, precursors.



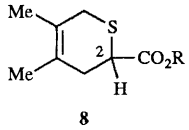
Thioaldehydes from *N*-phthaloylsulfenamides

Harpp and Back[5] found that methyl phthalimidosulfanylacetate **1b** and benzylamine reacted at room temperature to give phthalimide **3** (69%), *N*-benzylphthalimide (16%) and the thiooxamide $PhCH_2NH(CO)CSNHCH_2Ph$ (27%). They suggested that the last product was formed, in a complex manner, from methyl thioxoacetate **2b** [*cf.* eqn. (1)]. In contrast, simple *N*-(alkylsulfanyl)phthalimides, lacking the electron-withdrawing ester group, sulfenylated primary and secondary amines cleanly to give the corresponding *N*-alkylsulfenamides. They did not describe their preparation of the *N*-phthaloylsulfenamide **1b**, but the following procedures, based upon published methods, proved to be satisfactory.

The disulfide **4a** was heated in benzene with an equimolecular amount of *N*-bromophthalimide **5** [eqn. (2)].[6] After a variable induction period, bromine was formed and the ethyl ester **1a** was eventually isolated, typically in 70% yield based upon the *N*-bromophthalimide **5**. As implied by eqn. (2) a substantial amount of the disulfide **4a** remained in the reaction mixture. However, when the quantity of *N*-bromophthalimide was increased relatively to that of the disulfide, the product **1a** was more difficult to purify and the yield was not improved. The methyl ester **1b** was prepared likewise. With subsequent batches

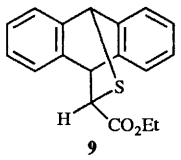
of the disulfide **4a** and *N*-bromophthalimide **5**, bromine was not liberated even after prolonged heating. However, addition of a catalytic amount of dibenzoyl peroxide initiated the reaction and led again to a satisfactory yield of the product **1a**. An alternative method[7,8] [eqn. (3)] was more reproducible. The *sulfenyl chloride* **6a**, prepared from ethyl mercaptoacetate, pyridine and sulfuryl chloride, was treated with potassium phthalimide **7** in dichloromethane to afford the ethyl ester **1a**, typically in 67% yield. Occasionally, the sulfenyl chloride **6a** was prepared from the disulfide **4a** and sulfuryl chloride. The methyl ester **1b** was also prepared by this method [eqn. (3)]. Both the thioxoacetate precursors **1a,b** were highly crystalline compounds (the sulfenyl chlorides **6a,b** are liquids) that could be stored without special precautions for extended periods. They dissolved easily in benzene and other common solvents.

The *N*-phthaloylsulfenamide **1a** was treated with triethylamine (1.2 mol equiv.) in benzene containing 2,3-dimethylbuta-1,3-diene (1 mol equiv.) at room temperature. The progress of the elimination reaction [eqn. (1)] to form ethyl thioxoacetate **2a** was indicated by the precipitation of phthalimide **3**. When all

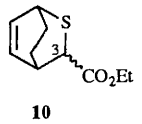


8

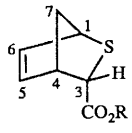
a R = Et
b R = Me
c R = H



9

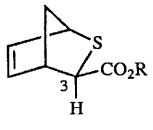


10

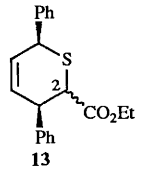


11

a R = Et
b R = Me



12



13

the precursor **1a** had disappeared (TLC control) the oily cycloadduct[1] **8a** was isolated (78%) from the reaction mixture. Similarly, the oily cycloadduct **8b** was obtained (85%) from **1b** and dimethylbutadiene and was identified by hydrolysis to give the known,[1] crystalline acid **8c**. Significantly, the ethyl ester **1a** and dimethylbutadiene did not react in the absence of triethylamine even when kept for 60 h in benzene at room temperature. Examination by TLC of the reaction mixtures containing the cycloadducts **8a,b** showed trace amounts of two by-products, judged by their R_F values to be the disulfides **4a,b** and the dithioester adducts **15a,b**; the possible origin of these by-products will be discussed later.

As expected, anthracene trapped the transient thioaldehyde **2a** less efficiently than did dimethylbutadiene. Thus, when anthracene was heated with the ethyl ester **1a** (1 mol equiv.) and triethylamine (1.2 mol equiv.) in benzene under reflux, the cycloadduct[1] **9** was obtained (53%). No doubt, the yield could be improved by the use of a large excess of anthracene, as was found in experiments with the sulfenyl chloride **6a** (37% yield of **9** with 1 mol equiv. anthracene[1] and 61% with 5 mol equiv. anthracene[9]). Again, **1a**, triethylamine and cyclohexa-1,3-diene gave (61%) the oily cycloadducts[1] **10** as a mixture of stereoisomers (*endo*:*exo* ratio[8] *ca.* 7:1).

The preparative value of the new thioxoacetate precursor **1a** is best illustrated by the synthesis of the *endo* **11a** and *exo* **12a** cycloadducts of cyclopentadiene. When a mixture of cyclopentadiene and triethylamine was treated with the sulfenyl chloride **6a**, in the usual way, a complex mixture was obtained from which only 19% of the cycloadducts **11a** and **12a** was isolated. Apparently, direct attack of the sulfenyl chloride on the diene had competed with the elimination [eqn. (1)] to form the thioaldehyde **2a**. In contrast, treatment of the phthalimido precursor **1a** with triethylamine, as before, in the presence of cyclopentadiene (1 mol equiv.) gave the cycloadducts **11a** and **12a** essentially quantitatively (*endo*:*exo* ratio *ca.* 7:3). The oily cycloadducts were separated on silica plates and identified by the ^{1}H NMR signals for 3-H; characteristically, that for the *endo* adduct **11a** [δ 4.42 (d, J 4.2 Hz)] appeared downfield of that for the *exo* adduct **12a** [δ 3.30 (br s)] and showed doublet splitting by 4-H. They were further characterised by hydrolysis to the corresponding, crystalline acids, **11b** and **12b**. Since phthalimide **3** is only weakly acidic (pK_a 8.3)[10] and eventually crystallises out of reaction mixtures in benzene, triethylamine, as implied by eqn. (1), is effectively not consumed during the elimination and may be used in catalytic amounts. Thus, the preparation of the cycloadducts **11a** and **12a** was accomplished in high yield with only 0.1 mol equiv. of triethylamine, although a longer reaction time was then required. When the preparation was repeated with triethylamine (1.2 mol equiv.) in benzene containing CD_3OD (2% by volume), the cycloadducts **11a** and **12a** contained no deuterium, *i.e.* base-catalysed interconversion of the *endo* and *exo* adducts had not occurred. Also, the *endo*:*exo* ratio was not affected by extended reaction times and must therefore reflect simply the relative rates of cycloaddition.

When the kinetically determined mixture of **11a** (70%) and **12a** (30%), or each isomer separately, was heated in toluene under reflux, the same, *exo*-rich equilibrium mixture was obtained (**11a**:**12a** = *ca.* 3:7). This suggested that the cyclopentadiene adducts, like the anthracene adduct[1] **9**, might, by thermal dissociation, be used preparatively as a 'clean' source of ethyl thioxoacetate **2a**. Moreover, the only by-product, cyclopentadiene, would be easily removed by evaporation. Thus, the 'kinetic mixture' of **11a** and **12a** was heated with 2,3-dimethylbuta-1,3-diene (1.1 mol equiv.) in toluene under nitrogen at 120 °C (sealed tube). Evaporation of the toluene gave the dimethylbutadiene adduct **8a**, contaminated with a small amount of cyclopentadiene dimer. Distillation yielded the pure cycloadduct **8a** (82%). The value of the adducts **11a** and **12a** as auxiliary precursors of ethyl thioxoacetate **2a** was demonstrated further with (*E*,*E*)-1,4-diphenylbutadiene, which is known[11] to react with maleic anhydride 114 times more slowly than does 2,3-dimethylbuta-1,3-diene. The 'kinetic mixture' of **11a** and **12a** was heated under reflux in xylene containing 1,4-diphenylbuta-1,3-diene (1 mol equiv.) under a slow stream of argon to remove cyclopentadiene. Evaporation of the xylene gave a residue consisting largely of the adduct **13** as a mixture of stereoisomers. The major isomer (the stereochemistry was not determined) was separated chromatographically as an oil (48%). In contrast, treatment of 1,4-diphenylbuta-1,3-diene with **1a** and triethylamine under the usual conditions gave only a low yield (*ca.* 9%) of the stereoisomers **13**.

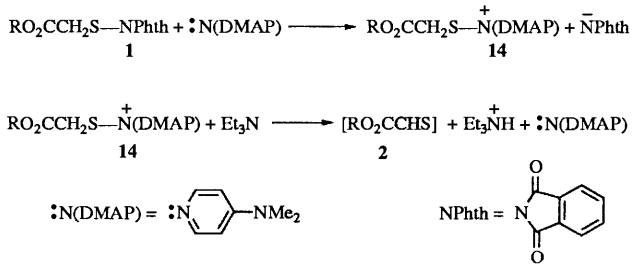
The cyclopentadiene adducts of ethyl thioxoacetate and other thioaldehydes have advantages over the corresponding anthracene adducts as auxiliary precursors of the thials; they are more easily prepared in high yield, especially from the Bunte salts[3] ZCH_2SSO_3Na, and give a volatile by-product, cyclopentadiene. However, with co-reactants of low reactivity reaction times may be much longer than for the anthracene cycloadducts because of the much higher rate of recapture of the thioaldehyde by cyclopentadiene. The use of cyclopentadiene cycloadducts in the synthesis of α-mercapto lactones[9] and thia-alkenolides[12] by intramolecular ene reactions has been reported. Vedejs *et al.*,[13] have also reported the preparation and synthetic applications of cyclopentadiene adducts of thioaldehydes generated photochemically from the phenacyl derivatives RCH_2SCH_2COPh. Although the elimination reaction [eqn. (1)] appears to be quantitative, capture of the thioaldehydes **2** by some co-reactant has to compete with polymerisation of the labile thials. If the reactivity of the co-reactant is low, better yields of useful products are obtained when the thioaldehydes are generated by the slow and reversible, retro-Diels–Alder

cleavage of the anthracene or cyclopentadiene adducts. In this way, the stationary concentration of the thioaldehyde is kept low, thereby retarding polymerisation; very likely the absence of any base in the reaction mixtures has the same, desirable effect.

Recently, Capozzi *et al.*,[14] have prepared a series of *N*-phthaloylsulfenamides $RCOCH_2SNPhth$, from the sulfenyl chloride PhthNSCl and enolisable ketones, and shown that they undergo elimination with pyridine to form the thioaldehydes RCOCHS, which were trapped *in situ* by conjugated dienes in the usual way. Several α-oxo thioketones were prepared similarly. Thus, a wider range of *N*-phthaloyl β-oxo sulfenamides is now available to serve as crystalline precursors for reactive thiono compounds.

Dithioesters from *N*-phthaloylsulfenamides

The dimethylbutadiene adduct **8a** and the cyclopentadiene adducts **11a** and **12a** (see above) were formed from the phthaloyl derivative **1a** and triethylamine in benzene containing CD_3OD (2% by volume) without incorporation of deuterium. Therefore, exchange of the methylene protons α to sulfur in **1a** did not precede the elimination reaction [eqn. (1)], nor did exchange of the methine protons α to sulfur take place in the cycloadducts. As expected, triethylamine is too weak a base to form significant amounts of carbanions stabilised only by one carbonyl group and one sulfur atom. Very likely, the elimination reaction involves an E2 mechanism. However, we cannot exclude the possibility that triethylamine first displaces the phthalimido group by nucleophilic attack on sulfur and then effects elimination of the quaternary ammonium intermediate $Et_3\overset{+}{N}SCH_2CO_2R$. Whether or not triethylamine acts in this way, the possibility that Steglich's base, 4-dimethylaminopyridine (DMAP), might effect nucleophilic catalysis (Scheme 1) of the elimination merited investigation.



Scheme 1

Triethylamine (1 mmol) and DMAP (0.1 mmol) in dichloromethane were added to the phthaloyl derivative **1a** (1 mmol) in dichloromethane containing 2,3-dimethylbuta-1,3-diene (1.2 mmol) at room temperature. The mixture soon became orange–red and phthalimide began to precipitate out. However, the major product (86% of the mixture, based upon **1a**) was the new dihydrothiine **15a**, which was accompanied by the expected cycloadduct **8a** (14%) and a trace of the disulfide **4a** (Table 1). As expected, the rate of disappearance of the precursor **1a** was greater than with triethylamine alone. Thus, DMAP had apparently effected nucleophilic catalysis, but the overall reaction had taken a different course. The major product **15a** could not arise by a secondary sulfenylation of the normal product **8a**, since triethylamine does not deprotonate the latter compound (see above). Apparently therefore, the initially formed thioaldehyde **2a** had been largely transformed into the α-oxo dithioester **16**, which was trapped as the cycloadduct **15a**. When the experiment was repeated with DMAP alone (1 mmol) the dithioester adduct **15a** was accompanied by only a small amount of the thioxoacetate adduct **8a**. Similar results were observed with benzene as the solvent. Pyridine was less effective than DMAP in forming the dithioester **16**, and the reaction mixtures then contained

Table 1 Base-mediated elimination of the thioxoacetate precursor **1a** in the presence of 2,3-dimethylbuta-1,3-diene (1.2 mol equiv.) at room temperature in dichloromethane

Base (mol equiv.)*	Rate order[b]	Products (%)[a] 8a	15a	4a
Et_3N (1)	2	100	Trace	Trace
Et_3N (1) + DMAP (0.1)	6	14	86	Trace
DMAP (1)	5	6	94	Trace
Et_3N (1) + Pyr (0.1)	3	84	3	13
Et_3N (1) + Pyr (0.5)	4	52	11	37
Pyr (1)	1	29	40	31

* DMAP = 4-dimethylaminopyridine. Pyr = pyridine. [a] Yields measured from the ^1H NMR spectra of crude, and base-washed product mixtures; no **1a** remained. [b] Order of increasing reaction rate (TLC monitoring); with pyridine the reaction required days, and with Et_3N + DMAP min, for completion.

Table 2 Base-mediated elimination of the thioxoacetate precursor **1a** in the presence of cyclopentadiene (2 mol equiv.) at room temperature in benzene

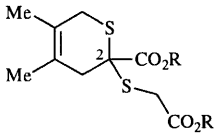
Base (mol equiv.)[b]	Products (%)[a] 11a + 12a[c]	17
Et_3N (1)	100	Trace
Et_3N (1) + DMAP (0.1)	68	32
DMAP (1)*	27	73

* DMAP = 4-dimethylaminopyridine. [a] Yields measured from the ^1H NMR spectra of crude, acid- and base-washed product mixtures. No disulfide **4a** was detected. [b] With pyridine (1 mol equiv.) the reaction was very slow, giving cyclopentadiene dimer and traces of **11a**, **12a** and **17** (TLC analysis). [c] **11a**:**12a** = *ca.* 7:3.

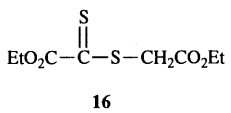
substantial amounts of the disulfide **4a**. The structure **15a** was deduced from the NMR spectra and mass spectrum. In particular, the ^1H NMR triplet for 2-H of **8a** was replaced by a sharp AB quartet for the side-chain, *S*-methylene group of the dithioester adduct **15a**, and signals for two ethoxy groups were observed in the spectrum of the latter. Hydrolysis of the oily adduct **15a** with aqueous sodium hydroxide gave the crystalline diacid **15c**, which gave good microanalytical data for C, H and S.

Whereas treatment of the phthaloyl derivative **1a** with triethylamine in the presence of cyclopentadiene gave the thioxoacetate adducts **11a** and **12a** essentially quantitatively, with triethylamine and 10% DMAP the dithioester adducts **17** were also formed, as an almost equal mixture of *endo* and *exo* isomers. However, the 'normal' adducts **11a** and **12a** were still the major products (Table 2). Even with DMAP alone (1 mol equiv.) substantial amounts of the adducts **11a** and **12a** were formed. It appeared therefore that the more reactive diene cyclopentadiene, which reacts with maleic anhydride 274 times faster than dimethylbutadiene,[11] had trapped ethyl thioxoacetate **2a** more efficiently than had dimethylbutadiene. This observation is good evidence that the intermediate dithioester **16** is formed from the thioxoacetate **8a** by a secondary process catalysed by DMAP.

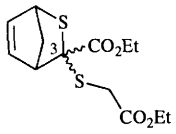
Simple dithioesters, RSCSR′, are familiar, stable compounds characterised by their deep magenta colours; they are poor dienophiles. Dithioesters with α carbonyl groups have occasionally been described in the literature,[15] and some appear to be unstable. As expected, the dienophilic character of the thiono group is greatly enhanced. For example, Vedejs *et al.*,[15b] prepared the derivative $MeSCSCO_2Et$ in the presence of dimethylbutadiene and isolated the corresponding Diels–Alder adduct **18**. The following experiments were designed to demonstrate the intermediacy of the dithioester **16** in the formation of the 'abnormal' products **15a** and **17**.



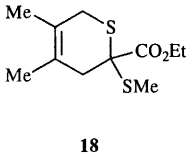
15
a R = Et
b R = Me
c R = H



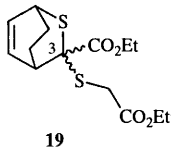
16



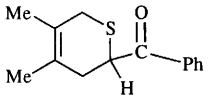
17



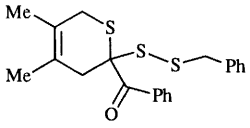
18



19



20



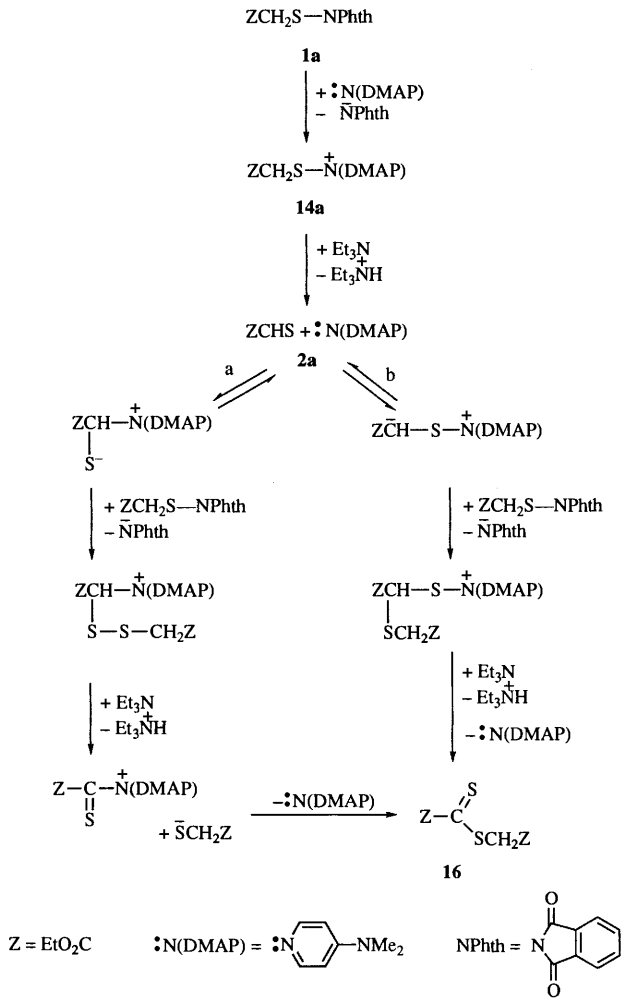
21

The phthaloyl derivative **1a** was treated with DMAP (1 mol equiv.) in dichloromethane at room temperature. The mixture rapidly became orange and then red and phthalimide began to precipitate out. The mixture was immediately shaken with dilute hydrochloric acid to remove the DMAP and then filtered to remove phthalimide. Evaporation of the dichloromethane gave a red oil, which was chromatographed to yield the dithioester **16** as a purple oil (56%), λ_{max}(EtOH)/nm 332 (ε/dm^3 mol^{-1} cm^{-1} 6176) and 515 (9.7). The ^{1}H and ^{13}C NMR spectra [δ_C 214.8 (C=S)] and the mass spectrum (accurate mass measurement for M^+) confirmed the structure **16**. Solutions of the dithioester were then treated separately at room temperature with cyclopentadiene, dimethylbutadiene and cyclohexa-1,3-diene to give, after chromatography, the corresponding cycloadducts **17** (87%), **15a** (88%) and **19** (67%). For preparative purposes, it was not necessary to isolate the dithioester **16**; fractions eluted from the chromatography column could be used directly, without evaporation, to form cycloadducts. Indeed, the stability of the oily dienophile **16** was critically dependent upon its purity, complete removal of DMAP during isolation being especially important. The rates of cycloaddition of **16** were assessed qualitatively by the disappearance of the purple colour. The rate order cyclopentadiene > dimethylbutadiene > cyclohexadiene corresponded with that recorded[11] for maleic anhydride with the same dienes (relative rates 698:2.5:1, respectively). The cyclopentadiene adducts **17** can serve as auxiliary precursors of the dienophilic dithioester **16**. When the adducts **17** (0.5 mmol) were heated in toluene (5 cm^3) under reflux with dimethylbutadiene (1 mmol), a pink colour quickly developed and then faded. After 4 h the mixture was evaporated to afford the adduct **15a** quantitatively.

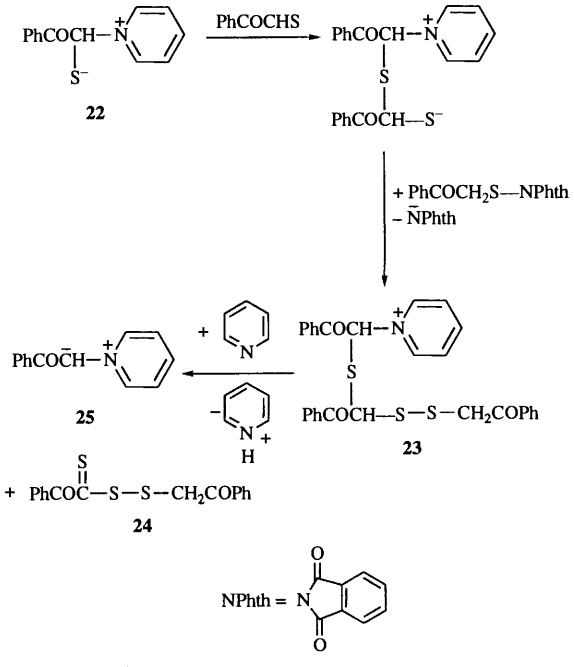
The thioaldehydes **2** and, to a lesser extent the dithioester **16**, are susceptible to oligomerisation or polymerisation. This process and its reversal were briefly studied. Triethylamine (1 mol equiv.) was added to the phthaloyl derivative **1a** in dichloromethane at room temperature. A precipitate of phthalimide appeared after a few seconds and examination of the mixture by TLC confirmed that the derivative **1a** reacts *faster* in the absence of any diene. The phthalimide was filtered off and the filtrate washed successively with aqueous sodium hydroxide and hydrochloric acid. The ^{1}H NMR spectrum of the product showed sharp signals attributed to the disulfide **4a** and broad signals (see the Experimental section) attributed to a polymer (oligomer) of **2a**. The experiment was repeated but the mixture was filtered as soon as the phthalimide had precipitated and the filtrate was immediately washed with hydrochloric acid. This time the product consisted almost entirely of the polymer (^{1}H NMR control). Treatment of this polymer with triethylamine or DMAP in the presence of dimethylbutadiene slowly gave the cycloadduct **8a** as the major product. Similarly, DMAP (1 mol equiv.) was added to the phthaloyl derivative **1a** in dichloromethane at room temperature. A pink colour developed but soon faded and phthalimide began to precipitate out. Again, the phthalimide was filtered off and the filtrate washed with hydrochloric acid to remove DMAP. Evaporation of the dichloromethane gave a polymeric residue containing only a small amount of the disulfide **4a**. Treatment of this polymer with triethylamine and dimethylbutadiene then slowly gave the dithioester adduct **15a** together with a little of the disulfide **4a** and a trace of the thioxoacetate adduct **8a**. Thus, the polymerisation (fast) of the thioaldehydes **2** and the dithioester **16** and the reverse process (slow) appears to be catalysed by base. When the polymer derived from **2a** was heated with dimethylbutadiene in chloroform in the absence of any base, no substantial amounts of the cycloadduct **8a** were formed. Finally, the purified dithioester **16** was kept at room temperature and the course of polymerisation monitored by the disappearance of the purple colour and by ^{1}H NMR spectroscopy. After 7 days, the spectrum of the colourless product showed broad signals for the polymer, whereas the sharp signals for the monomer had disappeared. However, after a further 7 days a new set of sharp signals (see the Experimental section) had largely replaced those of the polymer. The new signals may arise from a dimer or trimer; a stereoisomer of the latter would be expected to be the thermodynamically most stable oligomer of the dithioester **16**.

We earlier reported[8] the formation of selenoaldehydes, ZCHSe, and their Diels–Alder trapping *in situ* with conjugated dienes, by 1,2-elimination of selenenyl derivatives, ZCH_2SeX, mediated by triethylamine. The selenoxoacetate and other selenoaldehyde cycloadducts were often accompanied by the corresponding adducts of the diselenoesters, $ZCH_2SeCSeZ$, although DMAP was not employed in any of these experiments. Possible mechanisms for the formation of the diselenoesters were discussed. Similar considerations may be relevant to the reactions of **1a** with DMAP and triethylamine (Scheme 2). In brief, nucleophilic catalysis of the formation of the thioxoacetate **2a** by DMAP (*cf.* Scheme 1) may be followed by carbophilic (path a) or thiophilic (path b) attack of the latter on the thial group. The penultimate step of the carbophilic route (path a) liberates the thiolate ZCH_2S^-. The reaction of this with the phthaloylsulfenamide **1a** may account for the formation of the disulfide **4a** under certain conditions. Also, when the polymer derived from the thioxoacetate **2a** was depolymerised with DMAP in the presence of dimethylbutadiene (see above), the major product was **8a** not **15a**. This supports the proposal in Scheme 2 that **1a** has a secondary role in converting **2a** into **16**. Nevertheless, no unique mechanism can be confidently deduced from the experimental evidence so far.

The recent work by Capozzi *et al.*[14] provides an even more complex mechanistic puzzle. When they treated the phthalimido derivative $PhCOCH_2SNPhth$ with pyridine in the presence of dimethylbutadiene, the expected cycloadduct **20** (30%) was accompanied by the unprecedented product **21** (21%). The presence of 3 sulfur atoms in the latter was established unambiguously by X-ray crystallography. Clearly, 3 molecules of the thioaldehyde precursor must contribute towards the product **21**. An extension of the carbophilic route of Scheme 2 might accommodate this observation (Scheme 3). The intermediate **22** might react carbophilically with a 'second molecule of the thioaldehyde PhCOCHS before sulfenylation by the starting material gives the last intermediate **23**. Fragmentation to afford the dienophile **24** and the stabilised ylide **25** would complete the sequence.



Scheme 2



Scheme 3

Notwithstanding the mechanistic complexities of the foregoing reactions, *N*-phthaloyl α-oxo sulfenamides can serve under well defined conditions as valuable precursors of labile thioaldehydes and dithioesters and the corresponding cycloadducts with conjugated dienes.

Experimental

Mps were determined on a Kofler, hot-stage microscope. ^{1}H NMR spectra were obtained at 90 MHz with a Perkin-Elmer R-32 spectrometer and at 200 MHz with a Bruker WP spectrometer; ^{13}C spectra were obtained with the latter instrument. *J* Values are in Hz. IR spectra were recorded on either a Perkin-Elmer 580 or 257 spectrometer. Mass spectra were obtained by EI at 70 eV with an AEI MS9 instrument. Solutions in organic solvents were dried with $MgSO_4$. The bps recorded for Kugelrohr distillations are oven temperatures, not true, equilbrium bps.

Ethyl phthalimidosulfanylacetate 1a

From the disulfide 4a [eqn. (2)].[6] The disulfide **4a** (0.85 g, 3.6 mmol) and *N*-bromophthalimide **5** (0.81 g, 3.6 mmol) were stirred in dry benzene (9 cm^3) at room temperature. Bromine was soon liberated and after 2 h the mixture was evaporated. Hexane was added to the semi-solid residue and the resulting white solid (0.91 g) was collected and recrystallised from hexane to afford the *phthalimidosulfanylacetate* **1a** as fine needles (0.78 g, 82%), mp 76–82 °C (Found: C, 54.3; H, 4.3; N, 5.3; S, 12.2. $C_{12}H_{11}NO_4S$ requires C, 54.3; H, 4.2; N, 5.3; S, 12.1%); ν_{max}(KBr)/cm^{-1} 1785 (weak), 1740 and 1715; δ(200 MHz; $CDCl_3$) 1.20 (t, *J* 7.1, Me), 3.52 (s, SCH_2), 4.14 (q, *J* 7.1, OCH_2), 7.78–7.84 (2 H, m, ArH) and 7.90–8.02 (2 H, m, ArH); *m/z* 265 (M^+). A subsequent preparation on a larger scale (19 mmol) gave a lower yield (45%) of the product **1a** but a third experiment (40 mmol in 100 cm^3 benzene) gave 84%. With other batches of the disulfide and *N*-bromophthalimide, no liberation of bromine was observed even when the mixture was heated. The following procedure was then adopted. The disulfide **4a** (1.05 g, 44 mmol) and *N*-bromophthalimide (1.00 g, 44 mmol) were heated in dry benzene (10 cm^3) under reflux. When recrystallised dibenzoyl peroxide (*ca.* 10 mg) was added to the mixture, bromine was soon produced. After 20 min, the mixture was cooled and evaporated and the residue extracted with hot hexane. The extracts were set aside to cool, when the product **1a** crystallised out (0.78 g, 67%).

From the sulfenyl chloride 6a [eqn. (3)]. Ethyl mercaptoacetate (12.0 g, 100 mmol) and pyridine (7.90 g, 100 mmol) in tetrachloromethane (10 cm^3) were added to sulfuryl chloride (13.5 g, 100 mmol) in tetrachloromethane (50 cm^3) to give the sulfenyl chloride **6a**, as described by Woulfe and Miller.[7] The precipitate of pyridinium chloride was removed by decantation and the yellow, supernatant solution was diluted with dichloromethane and then treated at −10 °C with a suspension of potassium phthalimide (20 g, 108 mmol), as before,[7] to give the product **1a** (17.9 g, 67.5%). Alternatively, the disulfide **4a** was cleaved in tetrachloromethane with sulfuryl chloride (1 mol equiv.) at room temperature to form the sulfenyl chloride **6a**.

Methyl phthalimidosulfanylacetate 1b

Prepared from either the disulfide **4b** or the sulfenyl chloride **6b**, as described above for the ethyl ester, in similar yields, the *phthalimidosulfanylacetate* **1b** formed fine needles, mp 125–130 °C (from hexane) (Found: C, 52.35; H, 3.5; N, 5.6; S, 12.65. $C_{11}H_9NO_4S$ requires C, 52.6; H, 3.6; N, 5.6; S, 12.7%); ν_{max}(KBr)/cm^{-1} 1785 (weak), 1740 and 1715; δ(90 MHz; $CDCl_3$) 3.54 (s, CH_2), 3.73 (s, OMe) and 7.72–8.03 (m, ArH); *m/z* 251 (M^+).

Preparation of the cycloadduct 8a of dimethylbutadiene from the phthaloylsulfenamide 1a

The sulfenamide **1a** (600 mg, 2.26 mmol) in benzene (23 cm^3) containing 2,3-dimethylbuta-1,3-diene (185 mg, 2.26 mmol) was treated at room temperature with triethylamine (274 mg, 2.71 mmol). Phthalimide began to crystallise out after *ca.* 30 min and, after a further 3 h, the sulfenamide had all reacted

(TLC control). The mixture was filtered and the filtrate washed successively with aq. sodium hydroxide (1 mol dm^{-3}), hydrochloric acid (1 mol dm^{-3}) and water and then dried. Evaporation of the mixture gave an oil, which was chromatographed on a column of silica gel (TLC grade). Elution with hexane–ethyl acetate (8:2) gave the known[1] cycloadduct **8a** (78%); δ_H(200 MHz; $CDCl_3$) 1.28 (t, *J* 7.1, OCH_2Me), 1.71 (m, 4- and 5-Me), 2.46 (m, 3-H_2), 3.09 (m, 6-H_2), 3.62 (t, *J* 6.5, 2-H) and 4.19 (q, *J* 7.1, OCH_2Me); δ_C(50.3 MHz; $CDCl_3$) 13.9 (OCH_2Me), 19.1 and 19.8 (4- and 5-Me), 30.3 (C-3), 34.0 (C-6), 40.8 (C-2), 60.9 (OCH_2), 122.8 and 125.4 (C-4 and -5) and 171.4 (C=O). The ^1H NMR data agreed well with those recorded[1] at 90 MHz. The preparation was repeated successfully with dichloromethane in place of benzene as the reaction medium.

Methyl 4,5-dimethyl-3,6-dihydro-2*H*-thiine-2-carboxylate 8b

The foregoing preparation was repeated with the methyl ester **1b** replacing **1a** to yield the oily *cycloadduct* **8b** (85%) (Found: M^+, 186.0717. $C_9H_{14}O_2S$ requires *M*, 186.0715); ν_{max}(liq. film)/cm^{-1} 1735; δ_H(90 MHz; $CDCl_3$) 1.70 (br s, 4- and 5-Me), 2.35–2.55 (m, 3-H_2), 3.09 (m, 6-H_2), 3.60 (t, *J* 6.4, 2-H) and 3.70 (s, OMe). Hydrolysis with aq. ethanolic sodium hydroxide gave the crystalline acid **8c**,[1] mp and mixed mp 97–98 °C.

Ethyl 2-thiabicyclo[2.2.2]oct-5-ene-3-carboxylate 10

Treatment of cyclohexa-1,3-diene with the sulfenamide **1a** and triethylamine, as described for the preparation of the cycloadduct **8a**, gave the known[1] cycloadduct **10** (mainly the *endo* isomer) (61%), which was identified by its ^1H NMR spectrum.

Ethyl 9,10-dihydro-9,10-thiaethanoanthracene-11-carboxylate 9

The phthaloyl sulfenamide **1a** (100 mg, 0.38 mmol) and anthracene (67 mg, 0.38 mmol) were heated under reflux in benzene (4 cm^3) and treated dropwise with triethylamine (45.5 mg, 0.45 mmol) in benzene (1 cm^3). After 4 h work-up gave, after chromatography, the cycloadduct **9**[1] (53%), which was identified by its ^1H NMR spectrum.

Preparation of the cyclopentadiene cycloadducts 11a and 12a and the corresponding acids 11b and 12b from the phthaloyl sulfenamide 1a

The sulfenamide **1a** (1.00 g, 3.77 mmol) was treated with triethylamine (455 mg, 4.5 mmol) in dry benzene (40 cm^3) containing cyclopentadiene (250 mg, 3.77 mmol) at room temperature. The mixture was kept overnight and then filtered to remove phthalimide. The filtrate was treated as described for the preparation of the cycloadduct **8a** and the sole product (666 mg) was chromatographed on a silica gel (TLC grade) column. Elution with chloroform gave successively the oily cycloadducts **12a** and **11a**. *Ethyl* endo-2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-*carboxylate* **11a** (469 mg, 67.6%) had bp 95 °C (0.02 mbar, Kugelrohr distillation) (Found: M^+, 184.0544. $C_9H_{12}O_2S$ requires *M*, 184.0558); ν_{max}($CHCl_3$)/cm^{-1} 1730; δ(200 MHz; $CDCl_3$) 1.25 (t, *J* 7.1, Me), 1.59–1.68 (m, 7-H_2), 3.75 (m, 4-H), 4.08 (m, 1-H), 4.14 (q, *J* 7.1, OCH_2), 4.42 (d, *J* 3.9, 3-H), 5.88 (dd, *J* 3.2 and 5.4, 5- or 6-H) and 6.47 (dd, *J* 2.9 and 5.4, 6- or 5-H). *Ethyl* exo-2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-*carboxylate* **12a** (183 mg, 26.4%) had bp 95 °C (0.02 mbar, Kugelrohr distillation) (Found: M^+, 184.0559. $C_9H_{12}O_2S$ requires *M*, 184.0558); ν_{max}($CHCl_3$)/cm^{-1} 1730; δ(200 MHz; $CDCl_3$) 1.28 (t, *J* 7.1, Me), 1.68 (d, *J* 9.9, 7-H), 1.91 (d, *J* 9.9, 7-H), 3.29 (s, 3-H), 3.53 (br s, 4-H), 4.10 (br s, 1-H), 4.22 (q, *J* 7.1, OCH_2), 5.95 (dd, *J* 3.2 and 5.4, 5- or 6-H) and 6.38 (dd, *J* 2.8 and 5.4, 6- or 5-H).

Each of the foregoing esters was hydrolysed at room temperature with dil. aq. ethanolic sodium hydroxide to afford the endo-*carboxylic acid* **11b**, mp 102–104 °C (from hexane) (Found: C, 54.1; H, 5.3; S, 20.8. $C_7H_8O_2S$ requires C, 53.8; H, 5.2; S, 20.5%); ν_{max}(KBr)/cm[1] 3420, 1700 and 1690; δ_H(90 MHz; $CDCl_3$) 1.60–1.72 (m, CH_2), 3.80 (m, 4-H), 4.12 (m, 1-H), 4.46 (d, *J* 4.0, 3-H), 5.89 (dd, *J* 3.0 and 5.2, 5- or 6-H), 6.50 (dd, *J* 3.0 and 5.2, 6- or 5-H) and 8.78 (br s, OH, exch. with D_2O) and the exo-*carboxylic acid* **12b**, mp 102–103 °C (from hexane) (Found: C, 53.9; H, 5.2; S, 20.9. $C_7H_8O_2S$ requires C, 53.8; H, 5.2; S, 20.5%); ν_{max}(KBr)/cm^{-1} 3420 and 1705; δ(90 MHz; $CDCl_3$) 1.68 and 1.91 (ABq, *J* 10, with fine splitting), 3.34 (s, 3-H), 3.60 (m, 4-H), 4.18 (m, 1-H), 5.97 (dd, *J* 3.0 and 5.6, 5- or 6-H), 6.41 (dd, *J* 3.0 and 5.0, 6- or 5-H) and 11.0 (br s, OH, exch. with D_2O).

Retro-Diels–Alder reactions of the cyclopentadiene cycloadducts 11a and 12a

Thermal equilibration. The 'kinetic mixture' (*endo*:*exo* = *ca.* 7:3) of the cycloadducts **11a** and **12a**, prepared as before, or each isomer separately, was heated under reflux in toluene for 7 h to give the same, equilibrium mixture of **11a** and **12a** (*endo*:*exo* = *ca.* 3:7), essentially quantitatively.

Formation of the dimethylbutadiene cycloadduct 8a. The 'kinetic mixture' of **11a** and **12a** (1.4 mmol) and 2,3-dimethylbuta-1,3-diene (1.54 mmol) were heated in toluene (6 cm^3) under nitrogen at 120 °C (sealed tube) for 21 h. The mixture was evaporated to give the dimethylbutadiene adduct **8a** and a small amount of cyclopentadiene dimer. Kugelrohr distillation then gave the pure cycloadduct **8a** (82%).

Formation of the 1,4-diphenylbutadiene cycloadducts 13. The 'kinetic mixture' of **11a** and **12a** prepared, as described before, from the sulfenamide **1a** (1.13 mmol) and used without purification, was heated under reflux in xylene (15 cm^3) containing (*E*,*E*)-1,4-diphenylbuta-1,3-diene (1.13 mmol) for 24 h under a slow stream of argon to remove cyclopentadiene. Evaporation of the mixture gave a residue consisting largely of stereoisomers of the cycloadduct **13**. Chromatography on a silica gel column eluted with hexane–diethyl ether gave as the major product (probably the all-*cis* isomer resulting from *endo* addition) *ethyl* 3,6-*diphenyl*-3,6-*dihydro*-2H-*thiine*-2-*carboxylate* **13** (48%) as an undistillable oil (Found: M^+, 324.1196. $C_{20}H_{20}O_2S$ requires *M*, 324.1184); ν_{max}($CHCl_3$)/cm[1] 1728; δ(90 MHz; $CDCl_3$) 1.14 (t, *J* 7, Me), 3.54 (d, *J* 5.4, 2-H), 3.95 (m, 3-H), 4.12 (q, *J* 7, CH_2), 4.68 (m, 6-H), 5.90-6.25 (m, J_{vic} *ca.* 10, 4- and 5-H) and 7.22–7.48 (m, 3- and 6-Ph).

Ethyl 2-(ethoxycarbonylmethylsulfanyl)-4,5-dimethyl-3,6-dihydro-2*H*-thiine-2-carboxylate 15a and the corresponding dicarboxylic acid 15c. 4-Dimethylaminopyridine (122 mg, 1 mmol) in dichloromethane (2 cm^3) was added to a stirred solution of the phthaloyl sulfenamide **1a** (265 mg, 1 mmol) and 2,3-dimethylbuta-1,3-diene (98 mg, 1.2 mmol) in dichloromethane (10 cm^3) at room temperature. The mixture became red and a precipitate of phthalimide appeared. Thereafter the red colour faded as the sulfenamide **1a** was consumed (TLC control). After the mixture had become almost colourless, the work-up described for the preparation of the cycloadduct **8a** and chromatography of the product gave the *dithioester cycloadduct* **15a** as an oil (54%) (Found: M^+, 318.0957. $C_{14}H_{22}O_4S_2$ requires *M*, 318.0954); ν_{max}(liq. film)/cm^{-1} 1730 and 1734; δ_H(200 MHz; $CDCl_3$) 1.27 and 1.30 (2 × t, *J* 7.1, 2 × OCH_2Me), 1.70 and 1.73 (2 × br s, 4- and 5-Me), 2.47 and 2.89 (br ABq, *J* 18.1, 3-H_2), 2.79 and 3.39 (br ABq, *J* 17.0, 6-H_2), 3.54 and 3.59 (ABq, *J* 15.9, SCH_2) and 4.16 and 4.22 (2 × q, *J* 7.1, 2 × OCH_2); δ_C(50.3 MHz, $CDCl_3$) 14.0 and 14.15 (OCH_2Me), 19.2 and 20.1 (4- and 5-Me), 30.4 (C-3), 33.8 (C-6), 40.3 (SCH_2) 58.1 (C-2), 61.4 and 62.2 (OCH_2), 122.2 and 124.3 (C-4 and -5) and 169.8 and 170.0 (C=O).

Hydrolysis of the ethyl ester **15a** with aq. ethanolic sodium hydroxide at room temperature and, after acidification,

extraction of the mixture with chloroform gave the corresponding *dicarboxylic acid* **15c**, mp 172–174 °C (from ethanol) [a sample from another preparation had mp 160 °C (decomp.)] (Found: C, 45.8; H, 5.1; S, 24.3. $C_{10}H_{14}O_4S_2$ requires C, 45.8; H, 5.4; S, 24.4%); ν_{max}(KBr)/cm^{-1} 1710; δ_H[200 MHz; $(CD_3)_2CO$] 1.70–1.71 (br s, 2 × Me), 2.43 and 2.84 (br ABq, *J* 18, 3-H_2), 2.89 and 3.41 (br ABq, *J* 17, 6-H_2), 3.59 and 3.63 (ABq, *J* 15.7, SCH_2) and 10.1 (br s, OH).

Ethyl 3-(ethoxycarbonylmethylsulfanyl)-2-thiabicyclo[2.2.1]-hept-5-ene-3-carboxylate 17

4-Dimethylaminopyridine (460 mg, 3.77 mmol) in benzene was added to a stirred solution of the phthaloylsulfenamide (1.0 g, 3.77 mmol) and cyclopentadiene (500 mg, 7.58 mmol) in benzene (25 cm^3) at room temperature. The mixture became yellow (but not red, *cf.* the preparation of the cycloadduct **15a**) and a precipitate of phthalimide appeared. Work-up (see the preparation of the cycloadduct **8a**) gave a yellow oil (580 mg) containing (^{1}H NMR analysis) the cycloadducts **17** (73%) and **11a** and **12a** (27%). Chromatography on silica gel gave an oily mixture of the endo- and exo-3-CO_2Et *cycloadducts* **17** (*endo*:*exo* = 1.0:0.9) (61%) (Found: M$^+$, 302.0642. $C_{13}H_{18}O_4S_2$ requires *M*, 302.0646); ν_{max}(liq. film)/cm^{-1} 1732; δ_H(200 MHz; $CDCl_3$) (*endo*-3-CO_2Et) 1.28 or 1.29 (t, *J* 7.1, Me), 1.30 or 1.33 (t, *J* 7.2, Me), 1.75 (br d, *J* 9.8, 7-H), 1.95 (dt, *J* 9.8 and 2.2, 7-H), 3.59 and 3.60 (ABq, *J ca.* 15, SCH_2), 3.68 (m, 1- or 4-H), 4.08 (m, 4- or 1-H), 4.09–4.33 (m, OCH_2), 5.96 (dd, *J* 5.4 and 3.1, 5- or 6-H) and 6.56 (dd, *J* 5.4 and 2.9, 6- or 5-H); δ_H(*exo*-3-CO_2Et) 1.28 or 1.29 (t, *J* 7.1, Me), 1.30 or 1.33 (t, *J* 7.2, Me), 1.87 (dt, *J* 9.6 and 2.3, 7-H), 2.36 (br d, *J* 9.6, 7-H), 3.39 and 3.42 (ABq, *J* 15.3, SCH_2), 3.90 (m, 1- or 4-H), 4.09–4.33 (m, OCH_2 and 4- or 1-H), 6.17 (dd, *J* 5.4 and 3.3, 5- or 6-H) and 6.42 (dd, *J* 5.4 and 2.9, 6- or 5-H); δ_C(50.3 MHz; $CDCl_3$) (*endo* and *exo* isomers) 14.0 and 14.1 (Me), 35.3, 35.34, 50.0 and 52.15 (CH_2), 51.8, 53.25, 53.4 and 54.0 (CH), 61.5, 62.0 and 62.35 (OCH_2), 69.8 and 71.1 (C-3), 132.5, 132.9, 137.1 and 141.0 (CH) and 169.4, 169.5, 169.9 and 171.0 (C=O).

Diethyl 3-thia-2-thioxopentanedioate 16 and its cycloadducts 15a, 17 and 19

The phthaloylsulfenamide **1a** (2.00 g, 7.55 mmol) in dichloromethane (50 cm^3) was treated with 4-dimethylaminopyridine (DMAP) (0.92 g, 7.55 mmol) in dichloromethane (5 cm^3) at room temperature. The mixture quickly became orange then red and phthalimide precipitated out. The mixture was immediately shaken with dil. hydrochloric acid, to remove DMAP, and then filtered, to remove phthalimide. The aqueous layer was extracted with dichloromethane and the combined dichloromethane solutions were washed with water, dried and evaporated to yield a red oil. The oil was immediately chromatographed on a column of silica gel (TLC grade). Elution with hexane–ethyl acetate (8:2) gave a purple solution, which was evaporated to yield the *dithioester* **16** as a purple oil (496 mg, 2.10 mmol, 56%) (Found: M$^+$, 236.0159. $C_8H_{12}O_4S_2$ requires *M*, 236.0177); λ_{max}(EtOH)/nm 332 (ε/dm^3 mol^{-1} cm^{-1} 6176) and 515 (9.7); ν_{max}(liq. film)/cm^{-1} 1736; δ_H(200 MHz; $CDCl_3$) 1.29 (t, *J* 7.1, $CH_2CO_2CH_2$*Me*), 1.41 (t, *J* 7.1, $CSCO_2CH_2$*Me*), 4.08 (s, SCH_2), 4.21 (q, *J* 7.1, CH_2CO_2-CH_2Me) and 4.39 (q, *J* 7.1, $CSCO_2CH_2$Me); δ_C(50.3 MHz; $CDCl_3$) 13.9 and 14.0 (Me), 38.2 (SCH_2), 62.1 and 63.6 (OCH_2), 159.3 and 166.2 (C=O) and 214.8 (C=S).

The dithioester **16** was further characterised as the cycloadducts **17**, **15a** and **19**, as follows. The purple fractions from the foregoing chromatography were combined and aliquots (each containing 0.525 mmol) were treated separately with an excess (3.77 mmol) of cyclopentadiene, 2,3-dimethylbuta-1,3-diene and cyclohexa-1,3-diene. The mixtures were kept at room temperature until the purple colour had discharged, to yield the cycloadducts **17** (87% isolated after 2 min), **15a** (88% after 40 min) and **19** (67% after 15 h), respectively. *Ethyl* 3-(*ethoxycarbonylmethylsulfanyl*)-2-*thiabicyclo*[2.2.1]*oct*-5-*ene*-3-*carboxylate* **19** was obtained as an oily mixture of the *endo*- and *exo*-3-CO_2Et stereoisomers (*endo*:*exo* = 3:1) (Found: M$^+$, 316.0781. $C_{14}H_{20}O_4S_2$ requires *M*, 316.0803); the ^{1}H NMR spectrum (200 MHz; $CDCl_3$) showed many overlapping multiplets, including those, near δ 1.30 and 4.20, expected for the ethoxy groups; diagnostic signals were resolved at δ 3.41 (s, SCH_2, *endo* isomer), 6.31 (t, *J* 7.2, 5- or 6-H, *endo*), 6.36 (t, *J* 7.1, 5- or 6-H, *exo*), 6.50 (t, *J* 7.1, 6- or 5-H, *exo*) and 6.62 (t, *J* 7.5, 6- or 5-H, *endo*); δ_C(50.3 MHz; $CDCl_3$) (*endo* isomer) 14.0 and 14.1 (Me), 18.9, 28.6 and 34.25 (CH_2), 35.6 and 37.0 (CH), 61.6 and 61.7 (OCH_2), 65.6 (C-3), 133.0 and 136.3 (C-5 and -6) and 169.6 and 170.7 (C=O); δ_C(*exo* isomer) 14.0 and 14.1 (Me), 20.6, 28.8 and 34.2 (CH_2), 35.8 and 37.3 (CH), 61.5 and 62.1 (OCH_2), 66.7 (C-3), 131.8 and 132.2 (C-5 and -6) and 169.3 and 169.5 (C=O).

Retro-Diels–Alder cleavage of the cyclopentadiene cycloadducts 17 of the dithioester 16

The cycloadducts **17** (150 mg, 0.50 mmol) were heated under reflux in toluene (5 cm^3) containing 2,3-dimethylbuta-1,3-diene (82 mg, 1.0 mmol) for 4 h. A transient pink colour was observed. Evaporation of the mixture gave the pure dimethylbutadiene cycloadduct **15a** essentially quantitatively.

Polymerisation and depolymerisation of ethyl thioxoacetate 2a

Triethylamine (952 mg, 9.43 mmol) was added to the phthaloyl sulfenamide **1a** (2.50 g, 9.43 mmol) in dichloromethane (50 cm^3) at room temperature. The mixture was filtered immediately after phthalimide had precipitated (a delay led to the formation of the disulfide **4a**) and the filtrate was immediately washed with hydrochloric acid (1 mol dm^{-3}), to prevent any further reaction, then successively with dil. aq. sodium hydroxide and water. The solution was dried then evaporated to yield an oil (1.03 g); δ_H(90 MHz; $CDCl_3$) 1.30 (3 H, br t, *J* 7, Me), *ca.* 3.6 (0.78 H, m), 4.20 (2 H, br q, *J* 7, OCH_2), *ca.* 4.7 (0.14 H, m) and *ca.* 5.1 (0.08 H, m). Treatment of this polymer (oligomer) with either triethylamine or 4-dimethylaminopyridine, in dichloromethane containing an excess of 2,3-dimethylbuta-1,3-diene, at room temperature for 2 d gave the thioxoacetate cycloadduct **8a** as the major product. The polymer and the diene did not react in the absence of a base when heated in chloroform under reflux for 3 h.

Polymerisation and depolymerisation of the dithioester 16

The phthaloylsulfenamide **1a** (0.50 g, 1.89 mmol) was treated in dichloromethane with 4-dimethylaminopyridine (0.23 g, 1.89 mmol), as described above for the preparation of the dithioester **16**. However, the red reaction mixture was kept at room temperature until the colour had disappeared. Work-up gave an orange oil (0.12 g), which gave a ^{1}H NMR spectrum like that of the foregoing thioxoacetate polymer except that the 'multiplets' (clusters of singlets) accompanying the broad ethoxy signals differed somewhat in intensity and chemical shift. Treatment of this polymeric oil (100 mg) with triethylamine (90 mg) and 2,3-dimethylbuta-1,3-diene (70 mg) in dichloromethane (10 cm^3) overnight at room temperature gave the cycloadduct **15a** as the major product. Further, the oily dithioester **16**, purified by chromatography, was kept at room temperature in the absence of any base. After 7 d, the purple colour had disappeared and the signals in the ^{1}H NMR spectrum for the monomer **16** had been replaced by the broad multiplets shown by the foregoing polymer. However, after a further 7 d, the resulting, colourless solid gave strong, sharp signals [δ(200 MHz; $CDCl_3$) 1.30 and 1.41 (2 × t, *J* 7.1, Me), 3.79 (s, SCH_2) and 4.22 and 4.41 (2 × q, *J* 7.1, OCH_2)] superimposed on the now weaker, broad signals. It appeared that the polymer had slowly been converted largely into a more stable oligomer, probably a dimer or trimer.

Acknowledgements

We thank the SERC and the Loudon Bequest for financial support (to A. W. L. and S. W., respectively) and Dr M. J. Miller for experimental details in advance of publication (ref. 7).

References

1 C. M. Bladon, I. E. G. Ferguson, G. W. Kirby, A. W. Lochead and D. C. McDougall, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1541.
2 Preliminary communication: G. W. Kirby and A. W. Lochead, *J. Chem. Soc., Chem. Commun.*, 1983, 1325.
3 G. W. Kirby, A. W. Lochead and G. N. Sheldrake, *J. Chem. Soc., Chem. Commun.*, 1984, 922.
4 G. W. Kirby, A. W. Lochead and G. N. Sheldrake, *J. Chem. Soc., Chem. Commun.*, 1984, 1469.
5 D. N. Harpp and T. G. Back, *J. Org. Chem.*, 1976, **41**, 2498.
6 *Cf.* K. H. Büchel and H. Conte, *Chem. Ber.*, 1967, **100**, 1248.
7 S. R. Woulfe, H. Iwagami and M. J. Miller, *Tetrahedron Lett.*, 1985, **26**, 3891; S. R. Woulfe and M. J. Miller, *J. Org. Chem.*, 1986, **51**, 3133.
8 G. W. Kirby and A. N. Trethewey, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1913.
9 S. S.-M. Choi and G. W. Kirby, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3225.
10 *The Merck Index*, ed. S. Budavari, Merck and Co., Inc., Rahway, 11th edn., 1989, p. 1170.
11 J. Sauer, D. Lang and A. Mielert, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 268.
12 S. S.-M. Choi, G. W. Kirby and M. P. Mahajan, *J. Chem. Soc., Perkin Trans. 1*, 1992, 191.
13 E. Vedejs, T. H. Eberlein and R. G. Wilde, *J. Org. Chem.*, 1988, **53**, 2220; E. Vedejs, J. S. Stults and R. G. Wilde, *J. Am. Chem. Soc.*, 1988, **110**, 5452.
14 G. Capozzi, S. Menichetti, C. Nativi, A. Rosi and G. Valle, *Tetrahedron*, 1992, **48**, 9023.
15 (*a*) W. Thiel, H. Viola and R. Mayer, *Z. Chem.*, 1977, **17**, 366; (*b*) E. Vedejs, M. J. Arnost, J. M. Dolphin and J. Eustache, *J. Org. Chem.*, 1980, **45**, 2601.

Paper 5/07236K
Received 2nd *November* 1995
Accepted 22nd *December* 1995