Intramolecular Ene Reactions of Thioaldehydes Giving α-Mercapto Lactones

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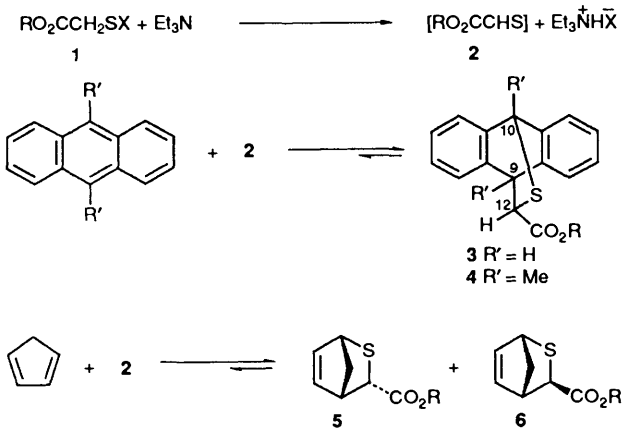
The crystalline acids **3b**, **4b** and **5b** and **6b**, formally cycloadducts of anthracene, 9,10-dimethylanthracene and cyclopentadiene, respectively, with thioxoacetic acid (HO_2CCHS), have been used to prepare esters with various allylic and homoallylic alcohols. These esters dissociated when heated, either in toluene under reflux or under the conditions of flash vacuum pyrolysis (FVP), to liberate transient thioaldehydes (thioxoacetate esters), which underwent intramolecular 'ene' reactions. Thus, the anthracene derivative **3c**, in toluene at 111 °C gave, *via* prenyl thioxoacetate **2c**, *cis*-2-mercapto-3-isopropenylbutyrolactone **13** in good yield. The corresponding cyclopentadiene derivatives **5c** and **6c** gave the same product, as a mixture of *cis* and *trans* isomers, essentially quantitatively when subjected to FVP. Similar experiments, involving Type [1,1] intramolecular ene reactions, gave the α-mercapto-γ-lactones **20**, **21** and **22**, and the epimeric α-mercapto-δ-lactones **26**. Further, the cyclopentadiene adduct **6h** of 2-methylprop-2-enyl thioxoacetate **2h** gave, under FVP conditions, the α-mercapto-δ-lactone **27** by a Type [2,1] ene reaction. Evidence supporting a concerted mechanism for the ene reactions is discussed.

Improved preparations of the cycloadducts **3b** and **4b** of thioxoacetic acid **2b** with anthracene and dimethylanthracene, respectively, are recorded.

The labile thioaldehyde, ethyl thioxoacetate **2a**, formed by 1,2-elimination from sulphenyl derivatives **1a**, has been trapped *in situ* as Diels–Alder adducts with various conjugated dienes (Scheme 1).[1] Moreover, the cycloadducts of anthracene[1] **3a**,

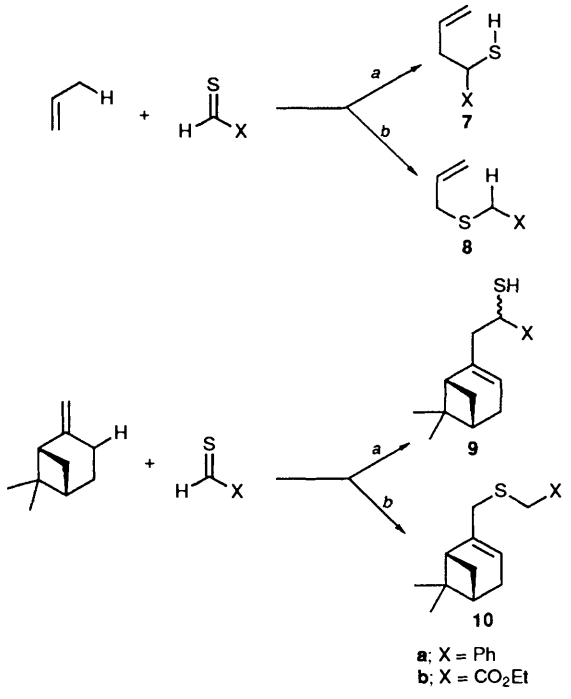


a; R = Et
b; R = H
c; R = $CH_2CH{=}CMe_2$
d; R = $CH_2CH\overset{Z}{=}CHMe$
e; R = $CH_2CH\overset{E}{=}CHMe$
f; R =


g; R = $CH_2CH_2CH{=}CMe_2$
h; R = $CH_2(Me)C{=}CH_2$

Scheme 1

9,10-dimethylanthracene[1] **4a** and cyclopentadiene[2,3] **5a** and **6a** dissociate at moderate temperatures (80–111 °C) and may thereby serve as convenient, auxiliary precursors of the thioaldehyde. The Diels–Alder reactions of thioaldehydes and the synthetic applications of the resulting cycloadducts have received considerable attention recently, notably through the investigations of Vedejs[4] and his co-workers. In contrast, the

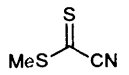


Scheme 2

corresponding ene reactions (Scheme 2) have been relatively neglected. We record here[5] our first survey of the intramolecular ene reactions of allylic and homoallylic thioxoacetate esters. The general synthetic strategy was modelled on that employed for *C*-nitroso formate esters.[6]

In principle (Scheme 2), ene reactions of thioaldehydes may proceed with C–C bond formation to give thiols **7** (pathway *a*) or with C–S bond formation to give sulphides **8** (pathway *b*). Both pathways have been observed for *intermolecular* ene reactions. Thus, thiobenzaldehyde[7] reacted with β-pinene to give the epimeric thiols **9a** (37%) and the sulphide **10a** (19%) whereas ethyl thioxoacetate[1] gave the corresponding products **10b** (78%) and **9b** (21%). Similarly, methyl thioxoacetate[8]

reacted with β-pinene, predominantly with C–S bond formation. In this respect, thioxoacetate esters resemble the dithioester[9] **11** and the thioketone[10] **12**, which react with β-pinene to form the corresponding sulphides (analogues of **10**)



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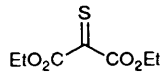

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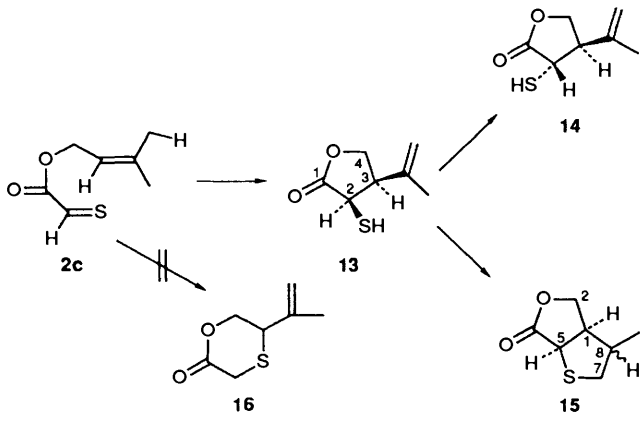
as the sole identified products. We expected that the outcome of intramolecular ene reactions of thioaldehydes would, however, be decided largely by conformational rather than electronic effects. Here we describe intramolecular reactions of thioxoacetate esters that lead exclusively to thiols (pathway *a*). A subsequent study[11] has shown how C–S bond formation may be achieved with ω-vinylalkyl thioxoacetate esters.

Results and Discussion

The crystalline acids **3b**, **4b**, **5b** and **6b** (Scheme 1) were used as 'masked' thioaldehyde units for the synthesis of the required thioxoacetate esters **2** from various allylic and homoallylic alcohols. Improved preparations of the anthracene acid **3b** (76%) and its 9,10-dimethyl derivative **4b** (61%), from the sulphenyl chloride[1] **1a** (X = Cl) are described in the Experimental section. A mixture of the cyclopentadiene adducts **5a** and **6a** was obtained, in high yield, most conveniently[3] with the Bunte salt **1a** (X = SO_3Na). The corresponding acids **5b** and **6b** were obtained separately by hydrolysis of the individual esters. Alternatively, the mixture of esters **5a** and **6a** (*ca.* 7:3) formed in the Diels–Alder reaction was hydrolysed to give a mixture of the acids **5b** and **6b**, which was used without separation. Generally, the required esters of unsaturated alcohols were obtained by treatment of the acids with *N,N'*-carbonyldiimidazole in tetrahydrofuran, or dichloromethane, followed by addition of the appropriate alcohol in the same solvent containing a catalytic amount of alkoxide generated with butyllithium. Generally, the *endo*- and *exo*-esters were separable by chromatography.

To confirm that the 3-methylbut-2-enyl ester **3c** would dissociate readily under the conditions previously found[1] for the ethyl ester **3a**, it was heated with 2,3-dimethylbuta-1,3-diene (10 mol equiv.) in toluene under reflux for 2.45 h. The corresponding cycloadduct of the diene was obtained in high yield (75% isolated) along with anthracene. No significant amount of the starting material **3c** was detected in the reaction mixture. Significantly, neither was any of the thiol **13** detected; this shows that an intermolecular Diels–Alder reaction of the thioaldehyde **2c** can proceed much faster than the intramolecular ene reaction, **2c**→**13**, which was observed, however, as follows. When the prenyl ester **3c** was heated alone under reflux in toluene under nitrogen for several hours (see below), efficient conversion into anthracene and the *cis*-thiol **13** was observed (Scheme 3). When air was not rigorously excluded the thiol was accompanied by a by-product **15**. This was presumably formed by radical cyclisation **13**→**15**, since the same cyclisation occurred when the thiol was heated in benzene with the radical initiator, azoisobutyronitrile. Initially, the constitution of the 2-mercaptobutyrolactone **13** was deduced by spectroscopic examination of its mixture with anthracene, formed directly from the cycloadduct **3c**. In particular, the butyrolactone ring was indicated by an IR band at 1780 cm^{-1}, and the thiol group by an NMR signal, δ 1.89 (d, *J* 4.5), which disappeared after exchange with deuterium oxide. Clearly, therefore, the intramolecular ene reaction had not occurred with C–S bond formation to form the thialactone **16**, although this might be favoured on electronic grounds alone. The *cis* stereochemistry **13** was established by treatment of the product with triethylamine in dichloromethane

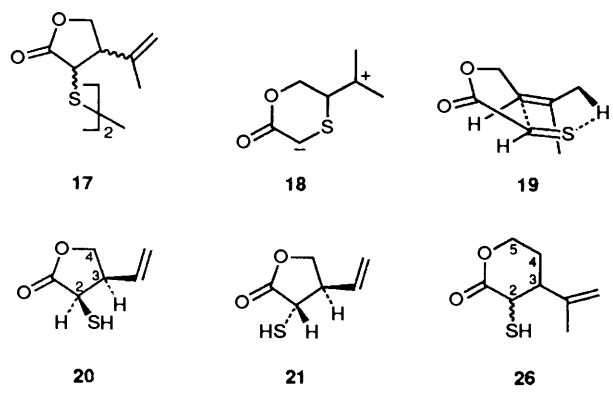


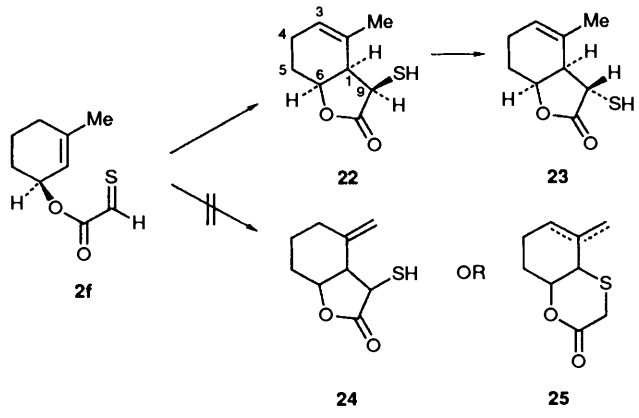
Scheme 3

at room temperature, to afford exclusively the *trans* epimer **14**. The corresponding change in the vicinal coupling constant $J_{2,3}$ from 7.1 to 9.5 Hz was that expected[12] for a 2,3-disubstituted butyrolactone. Confirmation of the relative stereochemistry of the epimers **13** and **14** was obtained from NOE experiments. Mutual enhancements of *ca.* 5% were observed upon sequential irradiation of the signals arising from 2- and 3-H in the *cis* epimer **13**, whereas no significant, corresponding enhancements were observed for the *trans* epimer **14**. Separation of the oily ene product **13** from anthracene on silica plates was readily accomplished, but was accompanied by partial epimerisation at C(2) and complete autoxidation to afford a gross mixture of disulphides **17** (in principle, 6 diastereoisomeric disulphides might arise from a mixture of the racemic thiols **13** and **14**). However, centrifugal chromatography on a silica plate under nitrogen (Chromatotron) afforded the *cis* thiol **13** as a colourless oil containing only a minor amount (*ca.* 10%) of the *trans* isomer **14**. For further characterisation, the *cis* thiol **13** was treated with benzoyl chloride and triethylamine to afford, with epimerisation, the crystalline *S*-benzoate of the *trans* isomer **14**. The corresponding *trans*-*S*-acetate was obtained as an oil.

The transformation **2c**→**13** is an example of a Type I intramolecular ene reaction,[13] according to the classification * of Oppolzer and Snieckus.[14] More precisely, Snider and Phillip's notation [15] would designate the thiol **13** as a Type [1,1] and the sulphide **16** as a Type [1,2] intramolecular ene product. The observed, preferential formation of the thiol **13** very likely reflects the energetically favourable, fused, [4.3.0]bicyclic transition state characteristic of a concerted Type [1,1] reaction. Concerted formation of the sulphide **16** would require a *bridged*, [3.3.1]bicyclic transition state. Further, if cyclisation of the thioaldehyde **2c** were to proceed stepwise, the presence of the electron-withdrawing carbonyl group should favour initial C–S bond formation (see above) giving an intermediate **18** and thence the product **16**. Evidence in favour of a concerted cyclisation of the thioaldehyde **2c** also came from parallel experiments with the (*Z*)- and (*E*)-crotyl esters **2d** and **2e**. In the *exo* transition state **19**,* leading to a *cis* product, hydrogen should be abstracted from the *pro*-*Z*-methyl group. In agreement with this, the anthracene adduct **3d** of the (*Z*)-crotyl ester **2d** gave, when heated in toluene, the expected *cis* thiol **20**, although the reaction was somewhat slower than that of the

* Reactions in which the enophilic component is attached, *via* a chain of atoms, to the allylic component, C(1)=C(2)–C(3)H, at either C-1, -2 or -3, are termed [14] Type I, II or III, respectively. Subclasses [15] arise since hydrogen may be transferred to the atom of the enophilic component remote from (subclass 1), or directly attached to (subclass 2), the connecting chain. A stereochemical classification is also sometimes employed. Thus the transition state **19**, of this Type I (or Type [1,1]) reaction, is termed *exo*.





Scheme 4

prenyl ester **3c**. In contrast, prolonged heating of the (*E*)-crotyl ester **2e** gave neither of the thiols **20** and **21**, nor any other detectable, ene product (a productive FVP experiment is described later). It appears, therefore, that the intramolecular ene reactions of thioxoacetates, and perhaps other thioaldehydes, are concerted, and controlled mainly by conformational rather than electronic effects. The oily *cis* thiol **20**, like its homologue **13**, was readily epimerised, and was characterised, after chromatography, as a mixture with the *trans* isomer **21** and as derivatives of the latter.

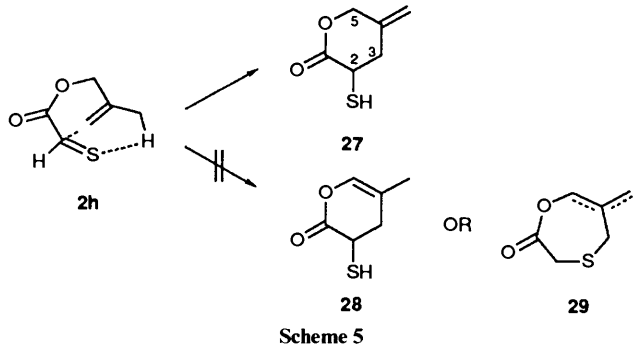
During repeated experiments on the thermolysis of the 3-methylbut-2-enyl derivative **3c** in refluxing toluene, it was noticed that the extent of reaction in a given time depended upon the initial concentration of the cycloadduct **3c**. Generally, the reaction proceeded faster in more dilute solutions, an observation of practical significance for preparative purposes. For example, when the cycloadduct **3c** was heated in toluene under reflux for 1 h under nitrogen at initial concentrations of 32 and 94 mmol dm^{-3} the corresponding extents of reaction, measured by ^1H NMR spectroscopy, were 63 and 36%. A similar observation was made earlier for the intramolecular ene reaction of nitrosoformate esters.[6] Although both the productive reactions, dissociation of the cycloadduct **3c** and the intramolecular ene reaction, are kinetically first-order, the overall process is retarded by fast, second-order recombination of the reactive intermediate **2c** with anthracene. As the reaction proceeds, the concentration of anthracene increases, causing a marked decrease in the overall rate. A detailed kinetic study was not made, but a simplified analysis of this reaction scheme, employing a steady-state approximation, indicated that a 3-fold increase in initial concentration should change the extent of reaction from 63 to *ca.* 40%, in reasonable agreement with observation. The corresponding cycloadduct **4c** of 9,10-dimethylanthracene (DMA) was also found to give the *cis* thiol **13** cleanly when heated in toluene. To discover whether thermolysis of this DMA adduct **4c** was significantly faster than that of the anthracene adduct **3c**, the adducts were heated separately in toluene under reflux at the same initial concentration (32 mmol dm^{-3}) for 1 h. The corresponding extents of reaction were 79 and 60%, respectively. However, this small rate advantage for the DMA adduct was not significant for preparative purposes, since anthracene is more readily available and less costly than its 9,10-dimethyl derivative. The latter is a superior 'trapping agent' for thioaldehydes, but in this study the unsaturated alcohols were each attached to the preformed, thioaldehyde 'synthons' **3b** and **4b**.

The cyclohexenyl derivative **2f** was selected to test further the regio- and stereo-specificity of the intramolecular ene reaction (Scheme 4). 3-Methylcyclohex-2-enol, required for the synthesis of the cycloadduct **3f**, is available commercially and can be readily made from *m*-cresol.[16] Thermolysis of the cycloadduct **3f** in toluene in the usual way proceeded cleanly to afford the bicyclic thiol **22** and anthracene. The ^1H NMR spectrum of the reaction mixture showed no significant signals attributable to other products such as the isomers **23**, **24** and **25**. Chromatography of the mixture under nitrogen (Chromatotron) gave the 1,9-*cis*-thiol **22** in crystalline form, m.p. 58–61 °C. Treatment with triethylamine at room temperature caused essentially complete inversion at C(9) and yielded the corresponding 1,9-*trans* isomer **23**, thus confirming the relative configuration of the ene product **22**. The presence of a γ-lactone ring, ν_{max} 1778 cm^{-1}, and a thiol group, δ 2.22 (d, *J* 4, SH, exchangeable with D_2O), in the product **22** were shown spectroscopically. Furthermore, an NMR signal, δ 5.77 (m), for only one olefinic proton excluded the alternative structures **24** from consideration. Both thiols **22** and **23** were characterised further as their *S*-acetyl derivatives. Thus, once more a Type [1,1] intramolecular ene reaction had occurred with the high regio- and stereo-selectivity expected of a concerted process.

Cyclopentadiene adducts, such as **5** and **6**, have advantages as auxiliary precursors of thioaldehydes over the corresponding adducts of anthracene **3** and DMA **4**. Cyclopentadiene is the most efficient, common trapping agent for thioaldehydes and is liberated as a highly volatile by-product when the cycloadducts are cleaved thermally. Thus, if thermolysis of the cycloadducts proceeds cleanly then the ene products may be isolated simply by evaporation of the solvent. However, the cycloadducts of cyclopentadiene dissociate more slowly than those of the aromatic dienes, anthracene and DMA. More seriously, the cyclopentadiene liberated during thermolysis will retard the overall reaction, by recombining with the thioaldehyde more rapidly than either anthracene or DMA. The likely magnitude of this effect is indicated by the reported[17] relative rates of the Diels–Alder reactions of maleic anhydride with cyclopentadiene and DMA at 30 °C (5.76:1), and with DMA and anthracene at 130 °C (218:1). These conclusions were borne out qualitatively by experiments with the 3-methylbut-2-enyl derivatives **5c** and **6c**. A mixture of the *endo* **5c** and *exo* **6c** adducts in toluene (11 mmol dm^{-3}) was heated as usual for 15 h. Conversion was incomplete, and a mixture of the adducts and the *cis* thiol **13** (*ca.* 2:1 as measured by ^1H NMR spectroscopy) was obtained. To achieve a greater conversion, the mixture of cycloadducts was heated for 15 h at 110 °C in xylene containing a small amount of the radical-chain inhibitor 2,6-di-*tert*-butyl-*p*-cresol, and nitrogen was passed slowly *through* the mixture to expel cyclopentadiene. In this way, a 63% conversion into the thiol **13** was observed, but the procedure was still inconveniently slow for preparative purposes. It was clear that flash vacuum pyrolysis (FVP)[18] offered a simple solution to the problem, since unimolecular dissociation and ene cyclisation could occur without competition from bimolecular recombination of the thioaldehyde and cyclopentadiene. This expectation was fully satisfied by the following experiments.

Dr. I. Gosney (University of Edinburgh) kindly provided his FVP apparatus for the first two experiments, those with the cyclopentadiene adducts **6c** and **6g**. The *exo* 3-methylbut-2-enyl adduct **6c** was evaporated slowly at 80 °C and *ca.* 0.01 mbar through a horizontal silica tube maintained at 600 °C. The products were collected in a trap cooled in liquid nitrogen then were allowed to warm to room temperature after addition of dichloromethane to the trap. Evaporation of the dichloromethane and cyclopentadiene gave the pure ene product as a mixture of the *cis* and *trans* isomers **13** and **14** (*ca.* 1:3) in nearly quantitative yield (95%). Presumably, partial epimerisation of the *cis* thiol had occurred in the hot tube, because even if direct formation of the *trans* isomer were to occur at high temperatures, its rate would be unlikely to exceed that for the *cis* isomer. Similarly, the homologous ester **6g** gave, under essentially the same conditions, the δ-lactone **26**, ν_{max} 1730 cm^{-1}, as a mixture of *cis* and *trans* isomers (*ca.* 1:9) in 62% yield. These results prompted the construction of an FVP apparatus in Glasgow based on the design recommended by Dr. Gosney. The pyrolysis of the *exo* prenyl cycloadduct **6c** was repeated, with essentially the same result; the thiols **13** and **14** (*ca.* 1:2) were obtained in *ca.* 100% yield. The less volatile anthracene cycloadduct **3c** was also successfully used as a precursor for the thioaldehyde **2c**; after it had been deposited on Celite to assist volatilisation. A suspension of Celite powder in dichloromethane containing the adduct **3c** was evaporated to give a dry powder. This was heated at 180 °C and *ca.* 10^{-5} mbar and the vapour of the adduct was allowed to pass as usual through the pyrolysis tube at 600 °C. Anthracene crystallised out on the walls of the tube between the furnace and the cold trap. The trap was found to contain the thiols **13** and **14** (*ca.* 2:3) (94%) and a little anthracene (6%). The pyrolysis of the homologous ester **6g** was also repeated, this time at the lower temperature of 500 °C. The yield of the δ-lactone **26** was improved to 99% and the mixture of stereoisomeric products contained less of the *trans* isomer (*cis–trans* ratio, 2:3) than before. Thus, it appears again that epimerisation of 2-mercapto lactones can occur in the pyrolysis tube.

To test the possibility of effecting a Type II intramolecular ene reaction, the *exo* cyclopentadiene adduct **6h** was subjected to FVP at 430 °C (Scheme 5). The reaction mixture was less

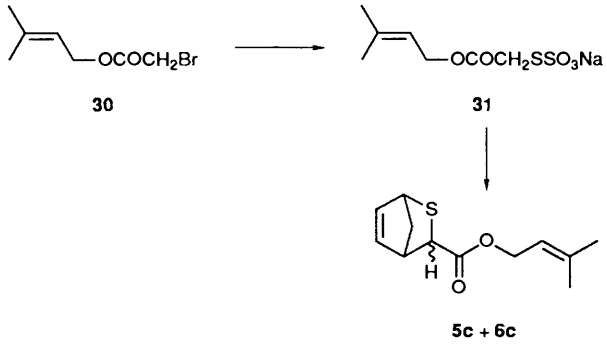


Scheme 5

clean (as judged by ^{1}H NMR spectroscopy) than those of the preceding pyrolyses; perhaps this reflects the energetically unfavourable, bridged, [3.3.1]bicyclic transition state required for a concerted Type [2,1] reaction (see formula **2h** in Scheme 5). The major product **27** (73%) was not accompanied by any substantial amounts of the isomers **28** or **29** (^{1}H NMR monitoring), but attempts to effect its purification by chromatography (Chromatotron) led to complete loss of material. Instead, the thiol was treated directly with methyl iodide and potassium carbonate to form the corresponding *S*-methyl derivative, which was stable to chromatographic purification.

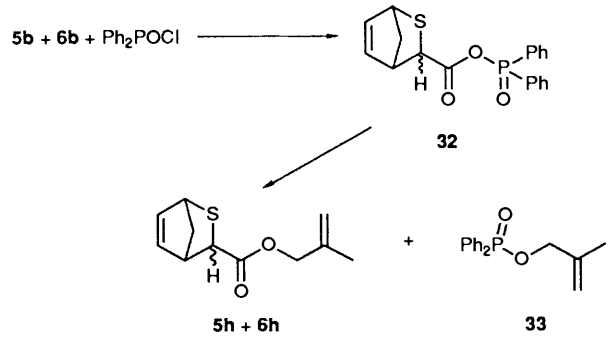
Although, as described earlier, the anthracene adduct **3e** of (*E*)-but-2-enyl thioxoacetate gave no ene product when heated in toluene, it was expected that the FVP technique would be productive. Indeed, pyrolysis of a mixture of the cyclopentadiene adducts **5e** and **6e** at 600 °C gave cleanly (*ca.* 100%) a mixture (*ca.* 1:1) of the thiols **20** and **21**. It is conceivable that the initially formed product was the *trans* isomer **21**, which then underwent isomerisation (*cf.* **2c**→**13** + **14**).

At the outset of these investigations, an alternative route was explored for the preparation of the cyclopentadiene adducts **5c** and **6c** (Scheme 6). The bromo acetate **30** was converted with



Scheme 6

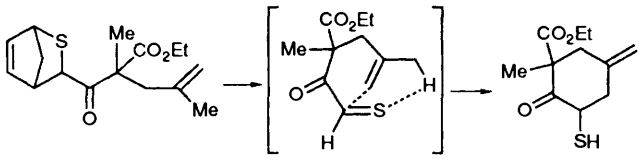
sodium thiosulphate, as usual, into the crystalline Bunte salt **31**. The bromo acetate and Bunte salt derived from 2-methylprop-2-en-1-ol were also prepared. Treatment of the salt **31** with triethylamine and calcium chloride in the presence of cyclopentadiene gave the required mixture of cycloadducts **5c** and **6c** in 75% yield. Clearly, the Diels–Alder trapping of the thioaldehyde **2c** was much faster than the ene cyclisation **2c**→**13**. Aqueous acetone was employed as the solvent, rather than the usual aqueous ethanol or methanol, to avoid any transesterification. Although this procedure was shorter, by one step, than the foregoing general method, the yield based upon the 3-methylbut-2-enyl alcohol was less, since this component was used in the first rather than the last step. For this reason, the method based upon the acids **5b** and **6b** is recommended generally. As explained before, the unsaturated esters of the cycloadduct acids **3b**, **4b**, **5b** and **6b** were generally prepared with *N*,*N*′-carbonyldiimidazole[19] as the condensing agent. On one occasion, an alternative method was tested. A mixture of the acids **5b** and **6b** was treated with diphenylphosphinoyl chloride[20] and *N*-methylmorpholine in dichloromethane to form the mixed anhydrides **32**, which were then heated with 2-methylprop-2-en-1-ol and triethylamine to give the required esters **5h** and **6h** (Scheme 7). The yield was satisfactory (70%),



Scheme 7

but chromatography was required to separate the cycloadduct esters from a small amount (*ca.* 6%) of the phosphinate ester **33**. Chromatography was not necessary when *N*,*N*′-carbonyldiimidazole was used; consequently diphenylphosphinoyl chloride was not employed on other occasions.

Vedejs *et al.*[21] have reported an independent study of the ene reactions of thioaldehydes, formed photochemically from the *S*-phenacyl derivatives of thiols. Significantly, productive reactions with β-pinene were not observed with aliphatic thioaldehydes lacking an electron-withdrawing α-carbonyl group. Further, an efficient Type [2,1] intramolecular ene reaction of an α-oxo thioaldehyde **35** was achieved in solution (Scheme 8) by thermolysis of the epimeric ketones **34** at 140 °C.



34 **35** **36**

Scheme 8

It is possible that geminal disubstitution in the thioaldehyde **35** facilitated the cyclisation **35**→**36** relative to that of the thioxoacetate ester, **2h**→**27** (Scheme 5). In conclusion, it is clear that the intramolecular ene reactions of thioaldehydes having α-ester or α-oxo groups, provide simple routes to cyclic products of synthetic potential. The resulting thiol groups may be removed reductively or by elimination, or used for further cyclisations, *e.g.* **13**→**15**. In principle, amides of the cycloadduct acids, *e.g.* **3b**, might serve as precursors for nitrogen-containing heterocycles. The formation of cyclic sulphides from ene reactions of thioxoacetate esters will be described in a later paper.[11] α-Alkylation of the cycloadduct **3a** has provided[22] a set of precursors for the corresponding thioketones $RCSCO_2Et$; suitably unsaturated derivatives of this type might also undergo intramolecular ene reactions, giving carbocyclic thiols.

Experimental

General.—M.p.s were determined with a Kofler, hot-stage apparatus. IR spectra were recorded on either a Perkin-Elmer 580 or 953 spectrometer. ^1H NMR spectra were obtained, except where otherwise stated, for solutions in deuteriochloroform, at 90 MHz with a Perkin-Elmer R34 spectrometer, or at 200 MHz with a Bruker WP 200 SY spectrometer. *J* Values are in Hz. Mass spectra were obtained by EI at 70 eV with AEI MS12 and MS9 spectrometers. Analytical TLC was carried out on commercial, precoated, Merck silica gel GF_{254} plates of thickness 0.25 mm. Compounds were revealed by UV light and iodine vapour. When exposed to iodine vapour, thiols initially gave white spots on a yellow background. Column chromatography employed Merck silica gel HF_{254} or 60H, the flow being assisted with a water pump.[23] Preparative TLC was carried out on Merck GF_{254} silica gel plates (20 × 20 × 0.05 cm), and centrifugal TLC (Harrison Chromatotron) under nitrogen on rotors coated with Merck silica gel PF_{254} (2 mm layers). Solutions in organic solvents were dried over magnesium sulphate and evaporated on a Büchi rotary evaporator. Unless otherwise stated, light petroleum refers to the fraction of b.p. 60–80 °C. High-boiling liquids were purified by Kugelrohr distillation; the cited b.p. is the oven temperature, not the equilibrium b.p.

Improved Preparation of the Anthracenecarboxylic Ester **3a** *and the Corresponding Acid* **3b**.*—*N*-Chlorosuccinimide was washed with water to remove succinimide, then was dried *in vacuo* over phosphorus pentoxide and recrystallised from benzene; the recrystallisation was less important than the aq. washing to ensure adequate purity. Ethyl mercaptoacetate (1.32 g, 11 mmol) was added to a stirred suspension of *N*-chlorosuccinimide (1.76 g, 13.2 mmol) in benzene (20 cm^3) at room temperature with exclusion of direct sunlight. A yellow colour, signifying the formation of the sulphenyl chloride, soon developed and succinimide began to crystallise out. After 2.5 h, the deep-yellow, supernatant solution (small amounts of succinimide do not interfere) was added dropwise to a stirred solution of anthracene (9.80 g, 55 mmol) in chloroform (140 cm^3) containing triethylamine (1.33 g, 13.2 mmol), which was being heated under reflux. Heating was continued for 30 min after the last addition of the sulphenyl chloride. The mixture was cooled and set aside to permit separation of anthracene, which was then filtered off. The filtrate was washed successively with dil. hydrochloric acid and water, then was dried and evaporated. The ester **3a**[1] (61%) was obtainable at this point by chromatography of the residue on a column of silica gel. To avoid the need for chromatography, the residue was treated in tetrahydrofuran (THF) (15 cm^3) or ethanol (15 cm^3) with aq. sodium hydroxide (1 mol dm^{-3}; 15 cm^3) with stirring at room temperature overnight. The mixture was evaporated to low volume, to remove most of the organic solvent, then was washed with dichloromethane (5 × 30 cm^3) to remove anthracene. The aq. solution was acidified with dil. hydrochloric acid, whereupon the carboxylic acid **3b** precipitated out (this precipitate was sufficiently pure for conversion into the ester **3a**, as described below). The mixture was extracted with diethyl ether (5 × 30 cm^3), and the extract was washed with brine, dried, and evaporated to give 9,10-*dihydro*-10,9-(*epithiomethano*)-*anthracene*-12-*carboxylic acid* **3b** (2.24 g, 76%), m.p. 182–183 °C (from diisopropyl ether or diethyl ether) (Found: C, 71.75; H, 4.5; S, 12.1%; M^+, 268.0557. $C_{16}H_{12}O_2S$ requires C, 71.6; H, 4.5; S, 12.0%; *M*, 268.0558); ν_{max}(KBr)/cm^{-1} 1710; δ_H(90 MHz) 4.16 (d, *J* 3, 12-H), 5.07 (d, *J* 3, 9-H), 5.18 (s, 10-H), 6.74 (br s, CO_2H, exch. with D_2O) and 7.09–7.43 (m, Ar-H). The carboxylic acid **3b** was kept in dry ethanolic hydrogen chloride (0.1 mol dm^{-3}) at room temperature overnight to form the ester **3a**, m.p. 136–137 °C (from diisopropyl ether) (lit.,[1] 135–137 °C), essentially quantitatively. When the esterification was carried out with heating under reflux some decomposition to form anthracene occurred.

Preparation of the 3-*Methylbut*-2-*enyl Ester* **3c** *and Other Unsaturated Esters* **3d–g** *of the Anthracenecarboxylic Acid* **3b**.—The acid **3b** (630 mg, 2.3 mmol) in dry THF (6 cm^3) was stirred for 3 h with *N*,*N*′-carbonyldiimidazole (400 mg, 2.5 mmol) at room temperature with exclusion of moisture, during which time carbon dioxide was seen to evolve. 3-Methylbut-2-en-1-ol (200 mg, 2.3 mmol) and butyllithium (0.3 mmol) in THF (1 cm^3) were then added. The mixture was stirred overnight at room temperature and then was evaporated. The residue was shaken with water and extracted with diethyl ether (4 × 20 cm^3). The combined extracts were washed with aq. sodium hydroxide (1 mol dm^{-3}; 10 cm^3) and then water (2 × 10 cm^3), and were dried and evaporated to give 3-*methylbut*-2-*enyl* 9,10-*dihydro*-10,9-(*epithiomethano*)*anthracene*-12-*carboxylate* **3c** as an oil (670 mg, 2.0 mmol, 85% (Found: M^+, 336.1192. $C_{21}H_{20}O_2S$ requires *M*, 336.1184); ν_{max}(liq. film)/cm^{-1} 1735 and 1677; δ(90 MHz) 1.64 and 1.72 (2 × br s, 2 × Me), 4.11 (d, *J* 2.0, 12-H), 4.52 (m, OCH_2), 5.07 (d, *J* 2.0, 9-H), 5.11 (s, 10-H), 5.27 (br t, *J* 7.0, $Me_2C{=}CH$) and 7.03–7.55 (8 H, m, Ar-H).

The other unsaturated esters **3** were prepared in a similar manner and yield from the acid **3b** and the appropriate alcohol with *N*,*N*′-carbonyldiimidazole as condensing agent either in THF or dichloromethane. Thus, (*Z*)-but-2-en-1-ol[24] gave (*Z*)-*but*-2-*en*-1-*yl* 9,10-*dihydro*-10,9-(*epithiomethano*)*anthracene*-12-*carboxylate* **3d**, m.p. 97–98 °C (Found: C, 74.4; H, 5.75; S, 10.2. $C_{20}H_{18}O_2S$ requires C, 74.5; H, 5.6; S, 10.0%); ν_{max}(KBr)/cm^{-1}

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1723; δ(90 MHz) 1.61 (d, *J* 6, Me), 4.09 (d, *J* 2.5, 12-H), 4.56 (m, OCH_2), 5.03 (d, *J* 2.5, 9-H), 5.07 (s, 10-H), 5.21–5.90 (2 H, m, vinyl-H) and 7.00–7.50 (8 H, m, Ar-H).

(*E*)-But-2-enol gave the (E)-*but-2-enyl anthracenecarboxylate* **3e** as an oil (Found: M^+, 332.1026. $C_{20}H_{18}O_2S$ requires *M*, 332.1027); $\nu_{max}(CHCl_3)/cm^{-1}$ 1732; δ(90 MHz) 1.62 (d, *J* 6, Me), 4.10 (d, *J* 2.5, 12-H), 4.35-4.52 (m, OCH_2), 5.05 (d, *J* 2.5, 9-H), 5.07 (s, 10-H), 5.22–5.90 (2 H, m, vinyl-H) and 7.00–7.55 (8 H, m, Ar-H).

3-Methylcyclohex-2-en-ol gave the corresponding ester **3f** as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1728; δ(90 MHz) 1.66 (br s, Me), 1.40–2.02 [6 H, m, $(CH_2)_3$], 4.08 (d, *J* 2, 12-H), 5.00–5.25 (m, vinyl-H), 5.02 (d, *J* 2, 9-H), 5.07 (s, 10-H), 5.24–5.46 (m, OCH) and 6.99–7.50 (8 H, m, Ar–H).

4-Methylpent-3-en-1-ol[25] gave the corresponding ester **3g**; δ(90 MHz) 1.57 and 1.68 (2 × br s, 2 × Me), 2.19 (br q, *J* 7, $CH_2CH{=}CMe_2$), 3.95 (t, *J* 7.5, OCH_2), 4.09 (d, *J* 2.5, 12-H), 4.9–5.2 (m, $CH{=}CMe_2$), 5.03 (d, *J* 2.5, 9-H), 5.07 (s, 10-H) and 6.90–7.60 (8 H, m, Ar-H).

Improved Preparation of the 9,10-*Dimethylanthracenecarboxylic Acid* **4b**.—Methyl mercaptoacetate (0.65 g, 6.1 mmol) was added dropwise to a stirred suspension of purified *N*-chlorosuccinimide (0.98 g, 7.3 mmol) in dichloromethane (10 cm^3) at room temperature (see the foregoing preparation of the acid **3b**). After 2 h, the resulting yellow solution of the sulphenyl chloride was added dropwise to a stirred solution of 9,10-dimethylanthracene[26] (1.27 g, 6.2 mmol) and triethylamine (0.74 g, 7.3 mmol) in dichloromethane (32 cm^3), which was being heated under reflux. Heating was continued for 30 min after the last addition of the sulphenyl chloride, then the mixture was cooled, washed successively with dil. hydrochloric acid and water, then was dried and evaporated. The residue was stirred with THF (20 cm^3) and aq. sodium hydroxide (1.3 mol dm^{-3}; 20 cm^3) at room temperature overnight. The mixture was washed with dichloromethane and then was acidified and extracted with diethyl ether (4 × 50 cm^3). The combined extracts were washed with brine, dried, and then were evaporated to afford the product **4b** (1.10 g, 61%) of sufficient purity for subsequent, direct use. 9,10-*Dihydro*-9,10-*dimethyl*-10,9-(*epithiomethano*)-*anthracene*-12-*carboxylic acid* **4b** had m.p. 171–173 °C (from diethyl ether) (lit.,[1] 173–175 °C) (Found: C, 73.0; H, 5.5; S, 11.3%; M^+, 296.0853. $C_{18}H_{16}O_2S$ requires C, 73.0; H, 5.4; S, 10.8%; *M*, 296.0871); $\nu_{max}(KBr)/cm^{-1}$ 1712; δ(90 MHz) 2.10 and 2.24 (2 × s, 2 × Me), 3.78 (s, 12-H), 7.07–7.45 (8 H, m, Ar-H) and 9.27–9.57 (br s, exch. with D_2O).

3-*Methylbut-2-enyl* 9,10-*Dihydro*-9,10-*dimethyl*-10,9-(*epithiomethano*)*anthracene*-12-*carboxylate* **4c**.—The carboxylic acid **4b** and *N,N'*-carbonyldiimidazole were treated in dichloromethane with a solution of 3-methylbut-2-en-1-ol in dichloromethane containing a catalytic amount of the corresponding lithium alkoxide, as described for the preparation of the corresponding anthracene derivative **3c**. The usual work-up gave a mixture of the required ester **4c** and a small amount of dimethylanthracene. Chromatography on silica gel gave the *methylbutenyl ester* **4c** as an oil (69%) (Found: M^+, 364.1521. $C_{23}H_{24}O_2S$ requires *M*, 364.1497); $\nu_{max}(CHCl_3)/cm^{-1}$ 1746; δ(90 MHz) 1.62 and 1.71 (2 × br s, $C{=}CMe_2$), 2.14 and 2.27 (2 × s, 9- and 10-Me), 3.83 (s, 12-H), 4.47 (br d, *J* 6, OCH_2), 5.24 (br t, *J* 6, vinyl-H) and 7.07–7.52 (8 H, m, Ar-H).

Preparation of the Unsaturated Esters **5c**, **e**, **g** *and* **h** *and* **6c**, **e**, **g** *and* **h** *of the Cyclopentadienecarboxylic Acids* **5b** *and* **6b**.—A mixture of the *endo*-**5a** and *exo*-**6a** cycloadducts of ethyl thioxoacetate and cyclopentadiene (**5a**–**6a** *ca.* 7:3) was prepared in the usual way[3] from the appropriate Bunte salt. They were separated by chromatography on silica gel as required. Hydrolysis of the esters together or separately gave the corresponding acids[2] **5b** and **6b**. The following esters were prepared, in good yields, from the appropriate alcohols with *N,N'*-carbonyldiimidazole as condensing agent, in the manner described for the anthracene derivatives **3**. 3-Methylbut-2-en-1-ol and a mixture of the acids **5b** and **6b** gave a mixture of the esters **5c** and **6c**, which was separated on a column of silica gel H_{254} eluted with chloroform–light petroleum (1:4 then 1:1) to give successively the *endo*-**5c** and *exo*-ester **6c**. 3-*Methylbut-2-enyl* 2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-endo-*carboxylate* **5c** was obtained as an oil, b.p. 110–120 °C (0.20–0.25 mbar) (Found: M^+, 224.0850. $C_{12}H_{16}O_2S$ requires *M*, 224.0871); ν_{max}(liq. film)/cm^{-1} 1734; δ(90 MHz) 1.62 (m, 7-H_2), 1.68 (br s, Me), 1.72 (br s, Me), 3.76 (br s, 1- or 4-H), 4.08 (br s, 4- or 1-H), 4.41 (d, *J* 4, 3-H), 4.56 (br d, *J* 7, OCH_2), 5.3 (br t, *J* 7, 2'-H), 5.86 (dd, *J* 5.5 and 3.0, 5- or 6-H) and 6.47 (dd, *J* 6.0 and 3.0, 6- or 5-H); the signals for 7-H_2 were obscured by those of the Me groups.

3-*Methylbut-2-enyl* 2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-exo-*carboxylate* **6c** also formed an oil, b.p. 105–110 °C (0.1 mbar) (Found: C, 64.2; H, 7.3%; M^+, 224.0863. $C_{12}H_{16}O_2S$ requires C, 64.3; H, 7.1%; *M*, 224.0871); ν_{max}(liq. film)/cm^{-1} 1736; δ(90 MHz) 1.63 and 1.93 (ABq, *J* 9.5, with fine splitting, 7-H_2), 1.70 (br s, Me), 1.73 (br s, Me), 3.29 (s, 3-H), 3.53 (br s, 1- or 4-H), 4.10 (br s, 4- or 1-H), 4.64 (br d, *J* 7, OCH_2), 5.38 (br t, *J* 7, 2'-H), 5.92 (dd, *J* 5.0 and 3.0, 5- or 6-H) and 6.37 (dd, *J* 5.5 and 2.5, 6- or 5-H).

(*E*)-But-2-en-1-ol and a mixture of the acids **5b** and **6b** gave the esters **5e** and **6e**, which were separated chromatographically as before. (E)-*But-2-enyl* 2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-endo-*carboxylate* **5e** was obtained as an oil (Found: M^+, 210.0692. $C_{11}H_{14}O_2S$ requires *M*, 210.0715); ν_{max}(liq. film)/cm^{-1} 1732; δ(90 MHz) 1.64 (m, 7-H_2), 1.68 (d, *J* 6.0, Me), 3.74 (m, 1- or 4-H), 4.07 (m, 4- or 1-H), 4.42 (d, *J* 4.0, 3-H), 4.50 (d, *J* 6.0, OCH_2), 5.34–6.02 (m, 2'- and 3'-H), 5.87 (dd, *J* 5.5 and 3.5, 5- or 6-H) and 6.47 (dd, *J* 5.8 and 2.5, 6- or 5-H).

(E)-*But-2-enyl* 2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-exo-*carboxylate* **6e** also formed an oil (Found: M^+, 210.0706. $C_{11}H_{14}O_2S$ requires *M*, 210.0714); ν_{max}(liq. film)/cm^{-1} 1730; δ(90 MHz) 1.67 and 1.90 (ABq, *J* 10, with fine splitting, 7-H_2), 1.70 (d, *J* 4.0, Me), 3.28 (s, 3-H), 3.54 (br s, 1- or 4-H), 4.10 (br s, 4- or 1-H), 4.57 (d, *J* 6.2, OCH_2), 5.37–6.07 (m, 2'- and 3'-H), 5.92 (dd, *J* 5.5 and 2.5, 5- or 6-H) and 6.37 (dd, *J* 5.3 and 2.5, 6- or 5-H).

4-Methylpent-3-en-1-ol[25] and a mixture of the acids **5b** and **6b** gave the esters **5g** and **6g**, which were separated chromatographically as before. 4-*Methylpent*-3-*enyl* 2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-endo-*carboxylate* **5g** was obtained as an oil (Found: M^+, 238.1032. $C_{13}H_{18}O_2S$ requires *M*, 238.1027); ν_{max}(liq. film)/cm^{-1} 1730; δ(90 MHz) 1.61 (br, s, Me), 1.68 (br s, Me), 1.61–1.81 (m, 7-H_2), 2.28 (br q, *J* 7.5, 2'-H_2), 3.73 (br s, 1- or 4-H), 4.02 (t, *J* 7.0, OCH_2), 4.07 (br s, 4- or 1-H), 4.40 (d, *J* 4.5, 3-H), 5.08 (br t, *J* 7.5, 3'-H), 5.86 (dd, *J* 5.5 and 3.0, 5- or 6-H) and 6.45 (dd, *J* 5.5 and 3.0, 6- or 5-H).

4-*Methylpent*-3-*enyl* 2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-exo-*carboxylate* **6g** also formed an oil (Found: M^+, 238.1026. $C_{13}H_{18}O_2S$ requires *M*, 238.1027); ν_{max}(liq. film)/cm^{-1} 1732; δ(90 MHz) 1.54–2.01 (m, 7-H_2), 1.61 (br s, Me), 1.67 (br s, Me), 2.31 (br q, *J* 7, 2'-H_2), 3.27 (s, 3-H), 3.50 (br s, 1- or 4-H), 4.08 (br s, 4- or 1-H), 4.10 (t, *J* 7.0, OCH_2), 5.10 (br t, *J* 7.5, 3'-H), 5.92 (dd, *J* 5.5 and 3.0, 5- or 6-H) and 6.36 (dd, *J* 5.8 and 3.0, 6- or 5-H).

2-Methylprop-2-en-1-ol and a mixture of the acids **5b** and **6b** gave a mixture of the esters **5h** and **6h**, which was separated chromatographically as before. 2-*Methylprop*-2-*enyl* 2-*thiabicyclo*[2.2.1]*hept*-5-*ene*-3-endo-*carboxylate* **5h** was obtained as an oil, b.p. 90–95 °C (0.1 mbar) (Found: C, 62.8; H, 6.9; S, 15.5%; M^+, 210.0717. $C_{11}H_{14}O_2S$ requires C, 62.8; H, 6.7; S, 15.2%; *M*, 210.0714); $\nu_{max}(CCl_4)/cm^{-1}$ 1740; δ(90 MHz) 1.66 (m, 7-H_2), 1.73 (br s, Me), 3.79 (m, 1- or 4-H), 4.10 (m, 4- or 1-H), 4.48 (d, *J* 2.5, 3-H), 4.50 (s, OCH_2), 4.94 and 4.98 (2 × br s, $C{=}CH_2$), 5.92

(dd, *J* 5.3 and 2.8, 5- or 6-H) and 6.49 (dd, *J* 5.5 and 2.5, 6- or 5-H).

2-Methylprop-2-enyl 2-thiabicyclo[2.2.1]*hept-5-ene-3-exo-carboxylate* **6h** also formed an oil, b.p. 90 °C (0.13 mbar) (Found: M^+, 210.0720. $C_{11}H_{14}O_2S$ requires *M*, 210.0714); ν_{max}(liq. film)/cm^{-1} 1738; δ(90 MHz) 1.67 and 1.93 (ABq, *J* 9, with fine splitting, 7-H_2), 1.77 (br s, Me), 3.34 (s, 3-H), 3.57 (m, 1- or 4-H), 4.02 (m, 4- or 1-H), 4.58 (br s, OCH_2), 4.95 and 5.01 (2 × br s, C=CH_2), 5.93 (dd, *J* 5.0 and 3.5, 5- or 6-H) and 6.39 (dd, *J* 5.5 and 2.5, 6- or 5-H).

Cycloadduct of 2,3-Dimethylbuta-1,3-diene and 3-Methylbut-2-enyl Thioxoacetate **2c**.—2,3-Dimethylbuta-1,3-diene (630 mg, 7.7 mmol) and the anthracene adduct **3c** (260 mg, 0.77 mmol) were heated under reflux in toluene (10 cm^3) for 2.45 h. The mixture was evaporated and the residue chromatographed on silica gel plates to give *3-methylbut-2-enyl 3,6-dihydro-4,5-dimethyl-2H-thiine-2-carboxylate* (140 mg, 75%) as an oil, b.p. 100–110 °C (0.1 mbar) (Found: M^+, 240.1205. $C_{13}H_{20}O_2S$ requires *M*, 240.1184); ν_{max}(liq. film)/cm^{-1} 1732; δ(90 MHz) 1.6–1.7 (m, CMe_2), 1.68 (br s, 4- and 5-Me), 2.44 (br d, *J* 6, 3- or 6-H_2), 3.08 (br s, 6- or 3-H_2), 3.60 (t, *J* 6.5, 2-H), 4.61 (d, *J* 7.5, OCH_2) and 5.35 (br t, *J* 7, vinyl-H).

Thermolysis of the Anthracene Ester **3c** *to give* cis-3-*Isopropenyl-2-mercaptobutan-4-olide* **13**.—The ester **3c** (0.37 g, 1.1 mmol) was heated under reflux in toluene (34 cm^3) under nitrogen. The reaction was judged to be complete (TLC control) after 4 h. Evaporation of the mixture gave anthracene and the butanolide **13**, which was judged by ^{1}H NMR spectroscopy to be a single, *cis* isomer. TLC on silica plates in air caused both epimerisation and oxidation to give a gross mixture of diastereoisomeric disulphides (see the main text). Chromatography under nitrogen on a Chromatotron (see general methods) in ethyl acetate–light petroleum (3:7) gave the cis-*butanolide* **13** and *ca* 10% of the *trans*-isomer **14** (0.12 g, 69%) (Found: M^+, 158.0409. $C_7H_{10}O_2S$ requires *M*, 158.0401); ν_{max}($CHCl_3$)/cm^{-1} 1780; δ(90 MHz) 1.76 (br s, Me), 1.89 (d, *J* 4.5, SH, exch. with D_2O), 3.30 (br q, *J* 7, 3-H), 3.87 (dd, *J* 7.1 and 4.1, 2-H), 4.40 (d, *J* 7.3, 4-H_2) and 4.74 and 5.05 (2 × br s, vinyl-H).

Epimerisation of the cis-*Thiol* **13**.—The foregoing *cis*-thiol **13**, prepared from the anthracene adduct **3c** (100 mg, 0.30 mmol), was kept in dichloromethane (10 cm^3) containing triethylamine (63 mg, 0.62 mmol) at room temperature for 3 h. The mixture was washed successively with dil. hydrochloric acid and water, and then was dried and evaporated to give the corresponding, oily *trans*-thiol **14**; ν_{max}($CHCl_3$)/cm^{-1} 1783; δ(90 MHz) 1.76 (br s, Me), 2.27 (d, *J* 4.7, SH, exch. with D_2O), 3.00 (br q, *J* 8, 3-H), 3.67 (dd, *J* 9.5 and 4.8, 2-H), 4.08 and 4.51 (2 × t, *J* 9, 4-H_2) and 4.94 and 5.00 (2 × br s, vinyl-H). The NMR signals were superimposable on those from the minor constituent of the foregoing mixture of *cis*- and *trans*-isomers.

trans-2-*Benzoylthio-3-isopropenylbutan-4-olide* (**14**; SCOPh *replacing* SH) *and the corresponding* S-*Acetyl Derivative*.—A mixture of the *cis*-thiol **13** and anthracene, obtained by thermolysis of the cycloadduct **3c** (0.26 g, 0.77 mmol), was stirred in chloroform (5 cm^3) containing triethylamine (0.11 g, 1.1 mmol) and benzoyl chloride (0.11 g, 0.78 mmol) at room temperature for 45 min. The mixture was diluted with chloroform (20 cm^3), washed successively with water, aq. sodium hydrogen carbonate and water, and then dried and evaporated. The residue was chromatographed on silica plates to afford the titled S-*benzoate* (**14**; SCOPh replacing SH) (0.10 g, 52%), m.p. 120–122 °C [from dichloromethane–light petroleum (b.p. 40–60 °C)] (Found: C, 63.9; H, 5.3; S, 12.3. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.3; S, 12.2%); ν_{max}(KBr)/cm^{-1} 1785 and 1666; δ(90 MHz) 1.81 (br s, Me), 3.31 (br q, *J* 10, 3-H), 4.16 (t, *J* 9.0, 4-H), 4.45 (d, *J* 11.0, 2-H), 4.52 (t, *J* 8.0, 4-H), 4.93 (br s, vinyl-H_2), 7.30–7.70 (m, *m*- and *p*-Ph-H) and 7.84–8.01 (m, *o*-Ph-H).

Similarly, acetylation of the *cis*-thiol **13** with acetic anhydride and triethylamine in chloroform gave the oily trans-S-*acetate* (**14**; SAc replacing SH) (Found: M^+, 200.0509. $C_9H_{12}O_3S$ requires *M*, 200.0507); ν_{max}($CHCl_3$)/cm^{-1} 1785 and 1705; δ(90 MHz) 1.80 (br s, vinyl-Me), 2.40 (s, Ac), 3.23 (br q, *J* 9, 3-H), 4.13 (t, *J* 9.6, 4-H), 4.28 (d, *J* 10.4, 2-H), 4.49 (t, *J* 8.8, 4-H) and 4.98 (m, vinyl-H_2).

When the acetylation was effected with acetic acid and dicyclohexylcarbodiimide in dichloromethane at room temperature, the *cis*-*S*-acetate (**13**; SAc replacing SH) was obtained as an oil; ν_{max}($CHCl_3$)/cm^{-1} 1780 and 1702; δ(90 MHz) 1.63 (s, vinyl-Me), 2.35 (s, Ac), 3.35 (ddd, *J* 8, 6 and 3, 3-H), 4.24 (dd, *J* 9 and 3, 4-H), 4.49 (dd, *J* 9 and 6, 4-H), 4.66 (d, *J* 8, 2-H) and 4.74 and 4.90 (2 × br s, vinyl-H). Attempted purification with a Chromatotron gave only the corresponding *trans*-*S*-acetate.

8-Methyl-3-oxa-6-thiabicyclo[3.3.0]*octan-4-one* **15**.—A mixture of the *cis*-thiol **13** and anthracene, obtained by thermolysis of the cycloadduct **3c** (160 mg, 0.48 mmol), was heated under reflux in benzene (15 cm^3) under nitrogen. Azoisobutyronitrile (9.2 mg, 0.056 mmol) was added, and heating was continued for 10 h. Evaporation of the mixture and chromatography of the residue (judged by ^{1}H NMR spectroscopy to contain the bicyclic lactone **15** and the thiol **13**, ratio *ca.* 4:1) on silica plates gave the *bicyclic lactones* **15** (44 mg, 58%), as an oily mixture of C-8 epimers (*ca.* 2:5) (Found: M^+, 158.0398. $C_7H_{10}O_2S$ requires *M*, 158.0401); ν_{max}(liq. film)/cm^{-1} 1780; δ(200 MHz) (major epimer) 1.09 (d, *J* 6.8, Me), 2.53–2.79 (m, 8-H), 2.82 (t, *J* 10.6, 7-H), 2.94 (dd, *J* 10.5 and 6.8, 7-H), 3.34 (tdd, *J* 8.8, 7.7 and 5.3, 1-H), 3.92 (d, *J* 7.7, 5-H), 4.08 (t, *J* 9.5, 2-H) and 4.29 (dd, *J* 9.5 and 8.8, 2-H); δ(200 MHz) (minor epimer) 1.13 (d, *J* 6.7, Me), 2.37 (septet, *J* 6.3, 8-H), 2.70 (dd, *J* 11.1 and 6.3, 7-H), 2.79–2.97 (m, 1-H), 3.14 (dd, *J* 11.0 and 5.7, 7-H), 4.00 (d, *J* 8, 5-H), 4.03 (dd, *J* 14 and 9.5, 2-H) and 4.40 (dd, *J* 9.5 and 7.5, 2-H); assignments of signals for 1-, 5- and 2-H are tentative owing to overlap with signals from the major epimer.

Thermolysis of the Anthracene Ester **3d** *to give* cis-2-*Mercapto-3-vinylbutan-4-olide* **20** *and its Epimer* **21**.—The cycloadduct **3d** (110 mg, 0.34 mmol) was heated under reflux in toluene (52 cm^3) under nitrogen for 8 h to give anthracene and the butanolide **20**, judged by ^{1}H NMR spectroscopy to be entirely (>90%) the *cis*-epimer. Separation with a Chromatotron under nitrogen, as described for the isopentenyl analogue **13**, gave an oily mixture (*ca.* 1:1) of the cis-*thiol* **20** and trans-*thiol* **21** (Found: M^+, 144.0250. $C_6H_8O_2S$ requires *M*, 144.0245); ν_{max}($CHCl_3$)/cm^{-1} 1772; compound **20**, δ (90 MHz) 1.91 (d, *J* 5.5, SH, exch. with D_2O), 3.32 (br quintet, *J* 7.5, 3-H), 3.80 (dd, *J* 7.5 and 5.0, 2-H), 4.29 (dd, *J* 7 and 5, 4-H_2), 5.20 (br d, *J* 17.5, CH=C*H*H), 5.29 (br d, *J* 10.0, CH=CH*H*) and 5.79 (ddd, *J* 17.5, 10.0 and 7.5, C*H*=CH_2); compound **21**, δ 2.23 (d, *J* 5, SH, exch. with D_2O), 2.74–3.20 (m, 3-H), 3.54 (dd, *J* 10 and 5, 2-H), 4.49 (dd, *J* 9.5 and 8.0, 4-H_2) and 5.10–6.08 (3 H, m, vinyl-H).

trans-2-*Benzoylthio-3-vinylbutan-4-olide* (**21**; SCOPh *replacing* SH).—Prepared from a mixture of the *cis*-thiol **20** and anthracene, with triethylamine and benzoyl chloride, in dichloromethane (as described for the analogous thiol **13**) the trans-S-*benzoate* (**21**; SCOPh replacing SH) was obtained as an oil (50%) (Found: M^+, 248.0519. $C_{13}H_{12}O_3S$ requires *M*, 248.0507); ν_{max}($CHCl_3$)/cm^{-1} 1786 and 1672; δ(90 MHz) 3.28 (br quintet, *J* 9, 3-H), 4.10 (t, *J* 9, 4-H), 4.30 (d, *J* 10.5, 2-H), 4.56 (t, *J* 8.5, 4-H), 5.22 (br d, *J* 9.5, CH=C*H*H), 5.24 (br d, *J* 17.5, CH=CH*H*), 5.82 (ddd, *J* 17.5, 9.5 and 7.5, C*H*=CH_2), 7.32–7.72 (m, *m*- and *p*-Ph–H) and 7.95 (m, *o*-Ph–H).

trans-2-(4-*Nitrobenzoylthio*)-3-*vinylbutan*-4-*olide* (**21**; 4-NO_2-C_6H_4S *replacing* HS).—Prepared in the way described for the *S*-benzoate, the titled trans-S-4-*nitrobenzoate* also formed an oil (Found: M^+, 293.0361. $C_{13}H_{11}NO_5S$ requires M, 293.0358); $\nu_{max}(CHCl_3)/cm^{-1}$ 1786 and 1678; δ(90 MHz) 3.32 (br quintet, *J* 10, 3-H), 4.14 (t, *J* 9.5, 4-H), 4.35 (d, *J* 11, 2-H), 4.59 (t, *J* 9, 4-H), 5.26 (br d, *J* 17.5, CH=C*H*H), 5.27 (br d, *J* 10, CH=CH*H*), 5.82 (ddd, *J* 17.5, 10 and 8, C*H*=CH_2) and 8.10 and 8.30 (2 × d, *J* 9, Ar-H).

Thermolysis of the Anthracene Ester **3f** *to give the* cis,cis-*Bicyclic Thiol* **22** *and therefrom Its* cis,trans-*Epimer* **23**.—The cycloadduct **3f** (270 mg, 0.75 mmol) was heated under reflux in toluene (24 cm^3) under nitrogen for 7 h to afford anthracene and the *cis,cis*-thiol **22**. Separation with a Chromatotron, as described for the isopentenyl derivative **13**, gave (1R*,6S*,9R*)-9-*mercapto*-2-*methyl*-7-*oxabicyclo*[4.3.0]*non*-2-*en*-8-*one* **22** as an oil (83 mg, 60%), which formed crystals, m.p. 58–61 °C [from dichloromethane–light petroleum (b.p. 40–60 °C)] (Found: C, 58.7, H, 6.8; S, 17.2%; M^+, 184.0550. $C_9H_{12}O_2S$ requires C, 58.7; H, 6.5; S, 17.4%; *M*, 184.0558; $\nu_{max}(CHCl_3)/cm^{-1}$ 1767; δ(90 MHz) 1.60–2.30 (m, 4- and 5-H_2), 1.77 (br s, Me), 2.22 (d, *J* 4, SH, exch. with D_2O), 3.18 (br t, *J* 8, 1-H), 3.88 (dd, *J* 9.0 and 4.0, 9-H), 4.50–4.86 (m, 6-H) and 5.77 (m, 3-H).

The *cis,cis*-thiol **22** was treated with triethylamine, as described for the *cis*-thiol **13**, to give (1*R**,6S*,9*S**)-9-mercapto-2-methyl-7-oxabicyclo[4.3.0]non-2-en-8-one **23** as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1765; δ(90 MHz) 1.72 (br s, Me), 1.55–2.25 (m, 4- and 5-H_2), 2.42 (d, *J* 4.5, SH, exch. with D_2O), 2.55–2.75 (m, 1-H), 3.55 (t, *J* 4.5, 9-H), 4.82–5.05 (m, 6-H) and 5.63 (m, 3-H).

Acetylation of the *cis,cis*-thiol **22** with acetic acid and dicyclohexylcarbodiimide in dichloromethane at room temperature, in the usual way, and purification of the product on a Chromatotron, gave the corresponding cis,cis-S-*acetate* (**22**; SAc replacing SH) as an oil (Found: M^+, 226.0664. $C_{11}H_{14}O_3S$ requires *M*, 226.0663); $\nu_{max}(CHCl_3)/cm^{-1}$ 1774 and 1703; δ(90 MHz) 1.63 (br s, 2-Me), 1.14–2.30 (m, 4- and 5-H_2), 2.42 (s, Ac), 3.32 (br t, *J* 8, 1-H), 4.59–4.92 (m, 6-H), 4.75 (d, *J* 9.5, 9-H) and 5.69 (br s, 3-H).

Acetylation of the *cis,trans*-thiol **23** with acetyl chloride and triethylamine in dichloromethane at room temperature, in the usual way, gave the corresponding cis,trans-S-*acetate* (**23**; SAc replacing SH) as an oil (Found: M^+, 226.0662. $C_{11}H_{14}O_3S$ requires *M*, 226.0663); $\nu_{max}(CHCl_3)/cm^{-1}$ 1776 and 1702; δ(90 MHz) 1.50–2.28 (m, 4- and 5-H_2), 1.80 (br s, 2-Me), 2.42 (s, Ac), 2.85 (br t, *J* 6, 1-H), 4.15 (d, *J* 5.5, 9-H), 4.62–5.08 (m, 6-H) and 5.66 (br s, 3-H).

Flash Vacuum Pyrolysis (FVP).—*General methods.* Pyrolysis of the cyclopentadiene cycloadducts **6c** and **6g**, described below, was first carried out in Edinburgh with the FVP apparatus constructed by Dr. I. Gosney. Similar apparatus, of a familiar design,[18] was used thereafter in Glasgow. Generally, cyclopentadiene cycloadducts were volatilised in a Büchi Kugelrohr oven at 80–110 °C, and the vapours were allowed to pass through a horizontal, silica tube (2.5 × 55 cm) at *ca.* 600 °C and *ca.* 10^{-3} mbar during *ca.* 10 min. The ene reaction products and cyclopentadiene were collected in a U-tube cooled in liquid nitrogen. Nitrogen was then admitted to the apparatus, and dichloromethane was added to the U-tube to facilitate removal of the products. The less-volatile, anthracene cycloadduct **3c** was pyrolysed as follows. A solution of the cycloadduct **3c** in dichloromethane was stirred with sufficient dry Celite powder to form a paste, which was then maintained under reduced pressure to produce a dry powder. The powder was heated in the FVP apparatus at 180 °C and *ca.* 10^{-5} mbar during 30 min, and the vapours were pyrolysed at 600 °C, as before. Anthracene crystallised out on the cool walls of the silica tube outside the furnace; a little also entered the U-tube with the ene product.

Preparation of the Butanolides **13** *and* **14** *by* FVP.—The cyclopentadiene cycloadduct **6c** was pyrolysed as described above, and the products, collected in the U-tube, were dissolved in dichloromethane. Evaporation of the mixture removed cyclopentadiene and left a mixture of the butanolides **13** and **14** (*ca.* 1:3) as a colourless oil (95%). No impurities were detected by ^1H NMR spectroscopy (90 MHz). A similar experiment was carried out with a mixture of the cycloadducts **5c** and **6c** (*ca.* 7:3), giving the butanolides **13** and **14** (*ca.* 1:2), again as a colourless oil (100%) (samples of the butanolide **13** formed by pyrolysis of the anthracene adduct **3c** in toluene were always obtained as pale yellow oils). FVP of the anthracene adduct **3c** likewise gave the butanolides **13** and **14** (*ca.* 2:3) as a yellow oil (94%).

Preparation of the Butanolides **20** *and* **21** *by FVP.*—FVP of a mixture of the cyclopentadiene cycloadducts **5e** and **6e** (*ca.* 1:1), as before, gave the butanolides **20** and **21** (*ca.* 1:1) as a colourless oil (100%). The products were identified by ^1H NMR spectroscopy (90 MHz).

Preparation of the Epimeric Pentanolides **26** *by* FVP.—FVP of the cyclopentadiene adduct **6g** at 500 °C gave 3-*isopropenyl*-2-*mercaptopentan*-5-*olide* **26** (*cis–trans* 2:3) as a colourless oil (99%) (Found: M^+, 172.0559. $C_8H_{12}O_2S$ requires *M*, 172.0558); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730; δ(200 MHz) 1.68 (br s, *cis*- and *trans*-Me), 1.73–2.25 (m, *cis*- and *trans*-4-H_2), 1.99 (d, *J* 4.5, *cis*-SH, exch. with D_2O), 2.42 (d, *J* 3.5, *trans*-SH, exch. with D_2O), 2.55 (dt, *J* 5.8 and 9.9, *trans*-3-H), 2.82 (dt, *J* 5.0 and 10.5, *cis*-3-H), 3.75 (dd, *J* 3.5 and 9.9, *trans*-2-H), 3.98 (ddd, *J* 1.2, 4.8 and 5.0, *cis*-2-H), 4.23 (td, *J* 11.5 and 4.1, *cis*-5-H), 4.32 (m, *trans*-5-H_2), 4.46 (ddd, *J* 2.5, 5.8 and 11.4, *cis*-5-H), 4.74 and 4.93 (2 × m, *cis*-C=CH_2) and 4.81 and 4.88 (2 × m, *trans*-C=CH_2). In a preliminary experiment, pyrolysis was carried out at 600 °C, but the product **26** (*cis–trans* 1:9) was obtained in lower yield (62%), and as a yellow oil.

Preparation of the Pentanolide **27** *by* FVP.—FVP of the cyclopentadiene adduct **6h** at 600 °C gave the pentanolide **27** as a yellow oil (52%) containing some unidentified impurities; $\nu_{max}(CHCl_3)/cm^{-1}$ 1726; δ(90 MHz) 2.42 (d, *J* 6, SH, exch. with D_2O), *ca.* 3 (m, obscured by signals from impurities, 3-H_2), 3.92 (dt, *J* 5.5 and 7.5, 2-H), 4.88 (br s, 5-H_2) and 5.04–5.27 (m, C=CH_2); *m/z* 144 (M^+). Attempted chromatography caused substantial loss of material. FVP of the adduct **6h** at 430 °C gave a better yield (73%) of the product **27**. The crude product was treated with iodomethane in dry acetone containing potassium carbonate. After 4 h at room temperature, the mixture was diluted with water and extracted with dichloromethane. Chromatography of the organic product on silica plates gave 2-*methylthio*-4-*methylenepentan*-5-*olide* (**27**; SMe replacing SH) (30% based upon the adduct **6h**) as an oil (Found: M^+, 158.0397. $C_7H_{10}O_2S$ requires *M*, 158.0402); $\nu_{max}(CHCl_3)/cm^{-1}$ 1718; δ(90 MHz) 2.24 (s, SMe), 2.70 (dd, *J* 4.5 and 17.0, with fine splitting, 3-H), 3.07 (dd, *J* 6.0 and 17.0, with fine splitting, 3-H), 3.57 (dd, *J* 4.0 and 5.8, 2-H), 4.78 and 5.14 (ABq, *J* 15.0, 5-H_2) and 5.10 (m, C=CH_2).

Sodium S-(3-*Methylbut*-2-*enyloxycarbonylmethyl*) *Thiosulfate* **31**.—Solutions of the bromoacetate[27] **30** (2.07 g, 10 mmol) in acetone (5 cm^3) and sodium thiosulfate pentahydrate (2.48 g, 10 mmol) in water (5 cm^3) were shaken together at room temperature for 15 min and then at *ca.* 40 °C for 2 min. By then, a homogeneous solution had formed and the reaction was judged by TLC to be complete. The mixture was evaporated, and the residue was dried *in vacuo* over phosphorus pentoxide

and then extracted with chloroform (2 × 30 cm^3). The extracts were filtered, and the filtrate was evaporated to give essentially pure product. The *Bunte salt* **31** (1.51 g, 58%) crystallised from acetone (Found: C, 31.95; H, 4.15; S, 24.6. $C_7H_{11}NaO_5S_2$ requires C, 32.1; H, 4.2; S, 24.4%); ν_{max}(KBr)/cm^{-1} 1740; δ(90 MHz; D_2O; standard Bu^{t}OH, δ 1.28) 1.76 (br s, Me), 1.81 (br s, Me), 3.94 (br s, CH_2S), 4.74 (br d, *J* 7.0, OCH_2) and 5.46 (br t, *J* 7.0, vinyl-H).

Sodium S-(2-*Methylprop*-2-*enyloxycarbonylmethyl*) *Thiosulfate*.—2-Methylprop-2-en-1-ol was treated in dichloromethane with bromoacetyl bromide and pyridine, in the usual way, to give 2-*methylprop*-2-*enyl bromoethanoate*, b.p. 120–130 °C (3 mbar) (Kugelrohr distillation) (Found: C, 37.65; H, 4.75; Br, 41.7. $C_6H_9BrO_2$ requires C, 37.3; H, 4.7; Br, 41.4%); ν_{max}(CCl_4)/cm^{-1} 1744; δ(90 MHz) 1.79 (br s, Me), 3.88 (s, $BrCH_2$), 4.62 (br s, OCH_2), and 4.99 and 5.03 (2 × br s, C=CH_2). This bromo ester was treated with sodium thiosulfate in aqueous acetone, as in the foregoing preparation, to give the corresponding *Bunte salt*, which was extracted from the dried product with hot ethanol and then crystallised from acetone (Found: C, 28.75; H, 3.2; S, 25.7. $C_6H_9NaO_5S_2$ requires C, 29.0; H, 3.6; S, 25.8%); ν_{max}(KBr)/cm^{-1} 1742 and 1708; δ (90 MHz; D_2O; standard Bu^{t}OH, δ 1.28) 1.82 (br s, Me), 4.02 (s, SCH_2), 4.70 (br s, OCH_2) and 5.09 (br s, C=CH_2).

Preparation of the Cyclopentadiene Cycloadducts **5c** *and* **6c** *from the Bunte Salt* **31**.—Triethylamine (301 mg, 3.0 mmol) was added slowly to a stirred suspension of the Bunte salt **31** (524 mg, 2.0 mmol), calcium chloride dihydrate (470 mg, 3.2 mmol) and cyclopentadiene (350 mg, 5.3 mmol) in acetone–water (7:1) (8 cm^3). Stirring was continued at room temperature for 24 h. The mixture was diluted with dichloromethane (50 cm^3) and the organic layer was washed successively with dil. hydrochloric acid and water, and was then dried and evaporated to afford a mixture of the cycloadducts **5c** and **6c** (330 mg, 74%).

Preparation of the Cyclopentadiene Cycloadducts **5h** *and* **6h** *from the Diphenylphosphinoyl Derivative* **32**.—The carboxylic acids **5b** and **6b** (*ca.* 7:3) (0.50 g, 3.2 mmol), diphenylphosphinoyl chloride (0.76 g, 3.2 mmol) and *N*-methylmorpholine (0.65 g, 6.4 mmol) were stirred in dichloromethane (6 cm^3) at −20 °C for 1 h with exclusion of moisture. The mixture was allowed to warm to room temperature, kept at this temperature for 30 min, and then heated under reflux for 1 min. 2-Methylprop-2-en-1-ol (0.23 g, 3.2 mmol) and triethylamine (0.65 g, 6.4 mmol) were added to the mixture and heating was continued for 14 h. The mixture was diluted with dichloromethane (40 cm^3) and then washed successively with water, dil. hydrochloric acid, water, dil. aq. sodium carbonate and water and then was evaporated to give an oil (0.54 g). The ^{1}H NMR spectrum of this product showed the presence of the cyclopentadiene esters **5h** and **6h** (*ca.* 1:1) (94%) and the phosphinate ester **33** (6%). Chromatography on a silica column gave the pure cycloadducts **5h** and **6h** (0.47 g, 70%) and 2-methylprop-2-enyl diphenylphosphinate **33** (34 mg) as a solid, which was not purified further (Found: M^+, 272.0959. $C_{16}H_{17}O_2P$ requires *M*, 272.0966); ν_{max}(KBr)/cm^{-1} 1440 and 1220; δ(90 MHz) 1.75 (s, Me), 4.42 (d, *J* 7, OCH_2), 4.92 and 5.05 (2 × br s, C=CH_2), 7.36–7.60 (m, Ph) and 7.67–8.02 (m, Ph).

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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 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 E. Vedejs, *Acc. Chem. Res.*, 1984, **17**, 358.
5 Preliminary communication: S. S-M. Choi and G. W. Kirby, *J. Chem. Soc., Chem. Commun.*, 1988, 177.
6 G. W. Kirby, H. McGuigan and D. McLean, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1961.
7 J. E. Baldwin and R. C. G. Lopez, *Tetrahedron*, 1983, **39**, 1487.
8 E. Vedejs, T. H. Eberlein and R. G. Wilde, *J. Org. Chem.*, 1988, **53**, 2220.
9 B. B. Snider, N. J. Hrib and L. Fuzesi, *J. Am. Chem. Soc.*, 1976, **98**, 7115.
10 G. W. Kirby and W. M. McGregor, *J. Chem. Soc., Perkin Trans. 1*, 1990, 3175.
11 S. S-M. Choi, G. W. Kirby and M. P. Mahajan, *J. Chem. Soc., Chem. Commun.*, 1990, 138.
12 D. Savastianoff and M. Pfau, *Bull. Soc. Chim. Fr.*, 1967, 4162.
13 D. F. Taber, *Intramolecular Diels–Alder and Alder Ene Reactions*, Springer, New York, 1984, ch. 3; W. Oppolzer, *J. Heterocycl. Chem.*, 1982, **19**, S-41.
14 W. Oppolzer and V. Snieckus, *Angew. Chem., Int. Ed. Engl.*, 1978, **17** 476.
15 B. B. Snider and G. B. Phillips, *J. Org. Chem.*, 1984, **49**, 183.
16 A. J. Birch, *J. Chem. Soc.*, 1946, 593.
17 J. Sauer, D. Lang and A. Mielert, *Angew. Chem.*, 1962, **74**, 352.
18 R. F. C. Brown, *Pyrolytic Methods in Organic Chemistry. Applications of Flow and Flash Vacuum Pyrolysis Techniques*, Academic Press, 1980.
19 H. A. Staab and W. Rohr, *Newer Methods of Preparative Organic Chemistry*, ed. W. Foerst, Academic Press, New York, 1968, vol. V, p. 72.
20 A. G. Jackson, G. W. Kenner, G. A. Moore, R. Ramage and W. D. Thorpe, *Tetrahedron Lett.*, 1976, **40** 3627.
21 E. Vedejs, T. H. Eberlein and R. G. Wilde, *J. Org. Chem.*, 1988, **53**, 2220.
22 G. W. Kirby, M. P. Mahajan and M. S. Rahman, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2033.
23 L. M. Harwood, *Aldrichimica Acta*, 1985, **18**, 25.
24 L. F. Hatch and S. S. Nabitt, *J. Am. Chem. Soc.*, 1950, **72**, 727.
25 H. Hirai and M. Matsui, *Agri. Biol. Chem.*, 1976, **40**, 169; L. Williman and H. Schinz, *Helv. Chim. Acta*, 1952, **35**, 2401.
26 G. W. Kirby and J. G. Sweeny, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3250.
27 B. B. Snider and J. W. van Straten, *J. Org. Chem.*, 1979, **44**, 3567

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