# α-Alkylation of the Diels–Alder Cycloadducts of the Thioaldehyde, Ethyl Thioxoacetate

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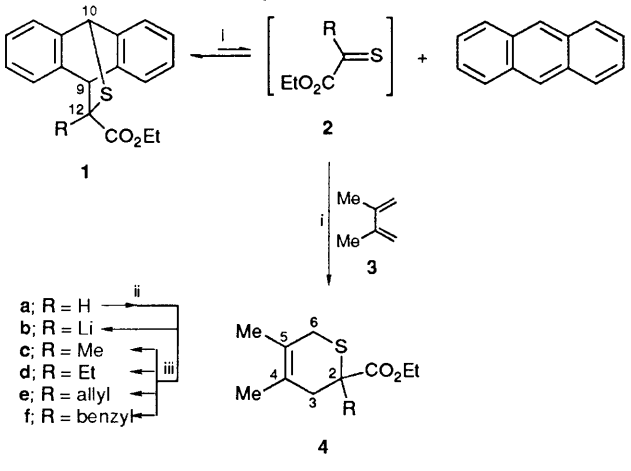
The cycloadduct **1a** of anthracene and the labile thioaldehyde, ethyl thioxoacetate **2a**, has been converted into the α-lithio derivative **1b** with lithium diisopropylamide (LDA). Subsequent treatment with, separately, methyl iodide, ethyl iodide, allyl bromide and benzyl bromide gave the corresponding 12-'alkyl' derivatives **1c–f**. Each derivative, when heated in toluene at 111 °C, dissociates to liberate anthracene and a thioketone **2**, which can be trapped *in situ* with 2,3-dimethylbuta-1,3-diene **3** to afford the corresponding 2-substituted dihydrothiine **4** in good yield. The same set of products **4** was obtained directly by α-alkylation of the parent dihydrothiine **4a**. Similarly, the 12-methyl anthracene adduct **1c** gives, with cyclopentadiene and cyclohexadiene, the stereoisomeric cycloadducts **5** and **6**, and **7** and **8** of the cyclic dienes and ethyl 2-thioxopropionate **2c**. When treated with LDA and methyl iodide, the thioaldehyde adducts **9a** and **13a** of cyclopentadiene and cyclohexadiene undergo rearrangement and *S*-methylation, rather than *C*-methylation, and afford the cyclopropanecarboxylates **10a** and **14a**. The methyl and ethyl sulphonium salts **17a–b** of the parent dihydrothiine **4a** rearrange similarly to give the cyclopropanecarboxylates **19a–b**. Methylation of the dilithio derivatives of the cycloadducts of thioxoacetic acid has also been investigated. The cyclopropanecarboxylic acid **14b** was found to rearrange slowly in the crystalline state to give the epimeric γ-lactones **15** and **16**.

We showed earlier [1] that the Diels–Alder adduct **1a** (Scheme 1) of anthracene and ethyl thioxoacetate **2a** dissociates, reversibly, in refluxing toluene and thereby serves as a stable, ancillary precursor for the labile thioaldehyde **2a**. For example, when heated with 2,3-dimethylbuta-1,3-diene (DMB) **3** the adduct **1a** gave the dihydrothiine **4a** in high yield, along with anthracene. It seemed likely that the corresponding cycloadducts of anthracene and thioketones (*e.g.* **2c–f**) would behave similarly and facilitate studies on the chemistry of these unstable species. With this in mind, we have investigated the alkylation of carbanions derived from various cycloadducts of ethyl thioxoacetate **2a**.

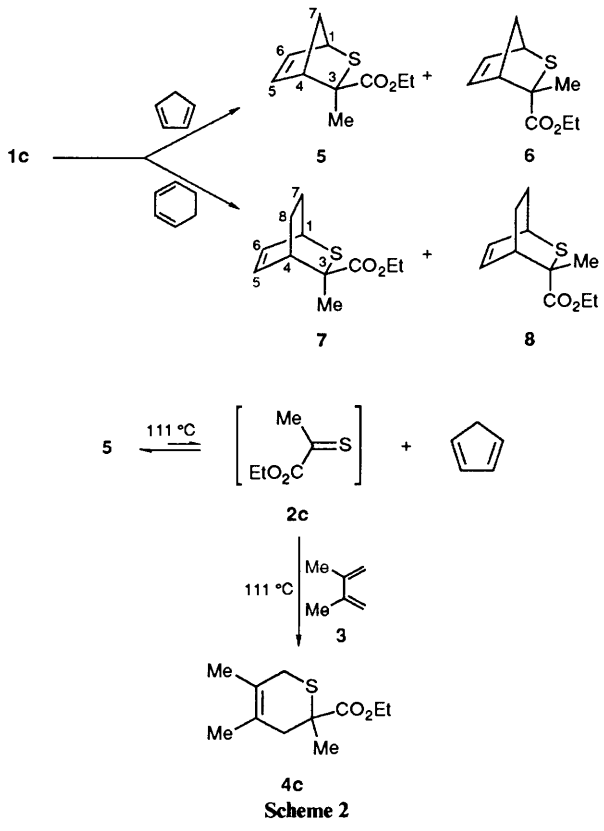



**Scheme 1** *Reagents and conditions:* i, 111 °C in PhMe; ii, LDA (1 equiv.) in THF at −78 to +20 °C; iii, MeI, EtI, $CH_2$=$CHCH_2Br$, or $PhCH_2Br$ (*ca.* 1.2 equiv.) at 20 °C for 3 h

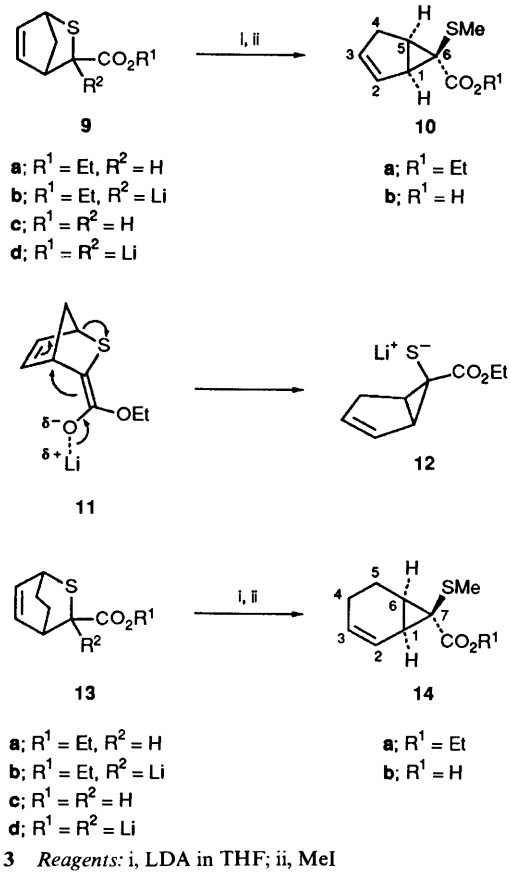
The lithium derivative **1b**, prepared from the cycloadduct **1a** with lithium diisopropylamide (LDA) in tetrahydrofuran (THF), reacted with methyl iodide to give the crystalline 12-methyl derivative **1c** in high yield (87%). Similarly, treatment of **1b** separately with ethyl iodide, allyl bromide, and benzyl bromide gave the corresponding, crystalline derivative **1d–f** efficiently. The oily, 2-substituted dihydrothiines **4c–f** were likewise obtained in high yield from the 2-lithio derivative **4b** of the thioaldehyde cycloadduct **4a** of DMB **3**. Hydrolysis of the methyl derivative **4c** gave the corresponding, crystalline carboxylic acid.

When the anthracene adducts **1c–f** were each heated with DMB in toluene under reflux for several hours, the corresponding DMB adducts **4c–f** were obtained, together with anthracene, in high yield. No by-products that might have arisen from competitive 'ene' reactions [1] were detected. Qualitative estimations of the rates of these thioketone 'transfer' reactions (TLC monitoring) indicated that they did not differ greatly from that of the parent thioaldehyde. This was verified, for the methyl thioketone, by a simple competition experiment. Thus, equimolecular amounts of the thioaldehyde **1a** and thioketone **1c** adducts and DMB were heated until the reactions were judged (TLC) to be complete (6 h). Analysis of the mixture of products by $^1H$ NMR spectroscopy showed that the dihydrothiines **4a** and **4c** were present in approximately equal amounts. Very little, if any, of the anthracene adducts **1a** and **1c** remained; this was consistent with the observed decomposition of the adducts **1a** and **1c–f**, to give anthracene and ill-defined polymers, when they were separately heated in the absence of DMB. As expected, when the 12-methyl cycloadduct **1c** was heated, under the foregoing conditions, in turn with cyclopentadiene and cyclohexa-1,3-diene, the corresponding cycloadducts **5** and **6**, and **7** and **8** of the dienes were obtained, again in high yield (Scheme 2). The cyclopentadiene adducts **5** and **6** were formed in a *ca.* 3:1 ratio, as measured by $^1H$ NMR spectroscopy. They were separated chromatographically, and identified by NMR spectroscopy. In particular, the 3-methyl protons in **5** resonated at a much higher field (δ 1.38) than those in **6** (δ 1.82), on account of shielding by the 5,6-double bond. The inseparable, cyclohexadiene adducts **7** and **8** were formed in approximately equal amounts. Again, the isomer **7** was identified in the mixture by the relatively high-field signal (δ 1.37) for the *endo* 3-methyl protons (δ 1.71 for **8**).

Earlier, we showed [2] that the *endo*- and *exo*-cycloadducts **9a** (Scheme 3) of cyclopentadiene and ethyl thioxoacetate



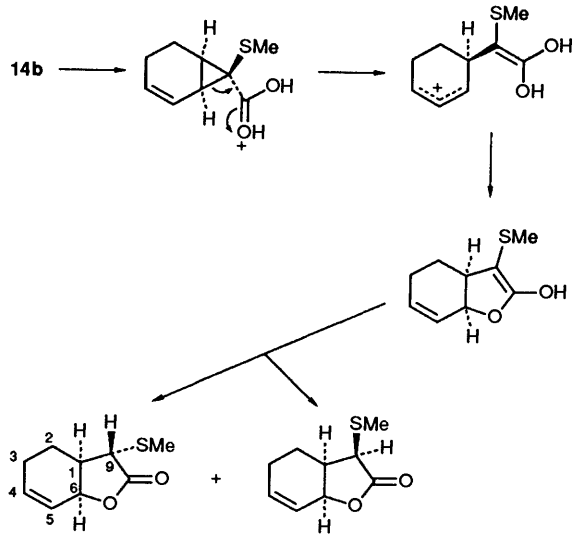
Scheme 2



Scheme 3 *Reagents:* i, LDA in THF; ii, MeI

dissociate when heated in toluene, and, like the anthracene adduct **1a**, may be employed as ancillary precursors of the thioaldehyde. The major cycloadduct **5** of the thioketone **2c** and cyclopentadiene was found to behave similarly. Thus, this cycloadduct **5** and dimethylbutadiene **3** (3 mol equiv.) were heated under reflux in toluene for 4 h (Scheme 2). Evaporation of the mixture gave the DMB adduct **4c** as the only significant product. Naturally, for preparative purposes there would be little point in forming cyclopentadiene cycloadducts from the corresponding anthracene cycloadducts, which are equally efficient precursors of thioketones (Scheme 1). However, a wide range of cycloadducts of cyclopentadiene may, in principle, be prepared by trapping, *in situ*, transient thioketones **2** formed, for example, by 1,2-elimination reactions of sulphenyl derivatives.[1,2,3] Nevertheless, we investigated α-alkylation of the *endo* and *exo* cycloadducts **9a** of ethyl thioxoacetate, since it might provide an alternative, general route to the corresponding thioketone adducts. Accordingly, a mixture of the stereoisomers **9a** was treated with LDA in THF at −78 °C (bath temperature) to form the lithio derivative **9b** (Scheme 3). Methyl iodide was added to the mixture, which was then allowed to warm up to room temperature. No significant amounts of the 3-methyl derivatives **5** and **6** were formed; instead the cyclopropane derivative **10a** was obtained in good yield. Clearly, rearrangement and *S*-methylation had occurred faster than *C*-methylation. The formation of the cyclopropanecarboxylate **10a** as a single stereoisomer, as judged from the NMR spectrum of the crude reaction mixture, may be explained by a concerted rearrangement, **11**→**12**, as shown in Scheme 3.* Similarly, attempted *C*-methylation of the lithio derivative **13b** of the cyclohexadiene adduct **13a** gave instead the cyclopropane derivative **14a**, again in good yield as a single stereoisomer.

The oily cyclopropanecarboxylic esters **10a** and **14a** were each hydrolysed with sodium hydroxide to provide the corresponding crystalline acids **10b** and **14b** for further characterisation. It was observed that a sample of the acid **14b** had largely decomposed after being stored at room temperature for several months. The $^1$H NMR spectrum of the decomposed sample indicated the presence of two lactones, **15** and **16**, in similar amounts (Scheme 4). These products were also prepared,



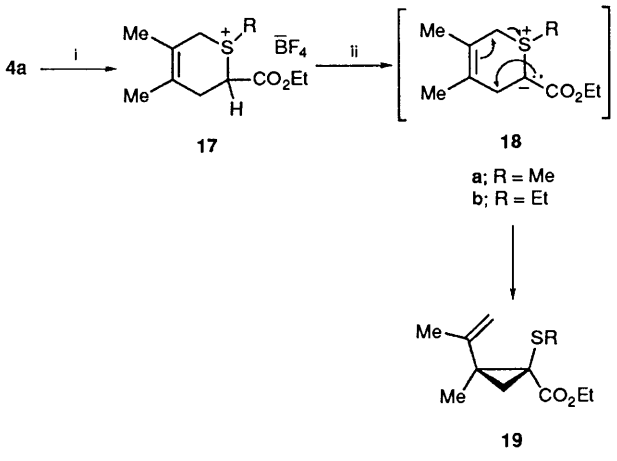
Scheme 4

for isolation and characterisation, by treatment of the acid **14b** with hydrochloric acid in chloroform; under these conditions the lactones were formed in the ratio **15**:**16** = *ca.* 2:1. Chromatography of the mixture gave the oily, major γ-lactone **15**, $\nu_{max}$/cm$^{-1}$ 1762, and the crystalline, minor γ-lactone **16**,

* We cannot however exclude the possibility that *S*-methylation of **9b** and **13b** may precede the rearrangements to form **10a** and **14a**.

$\nu_{max}$/cm$^{-1}$ 1764. The relative stereochemistry, including the *cis* ring fusion, of the epimeric lactones was deduced from the $^1$H NMR spectra. The vicinal coupling constants for the major epimer **15**, $J_{1,9}$ 3.9 Hz, and minor epimer **16**, $J_{1,9}$ 7.3 Hz, were consistent with the relative magnitudes of the relevant torsion angles observed in models. Presumably, acid-catalysed opening of the cyclopropane ring is facilitated by formation of an allylic carbocation (Scheme 4). In the crystalline state, protonation of the carboxy group must be effected by that in a neighbouring molecule; the two carboxy groups may already be connected by a hydrogen bond. In contrast, the related cyclopenteno acid **10b** remained unchanged after 30 days at room temperature.

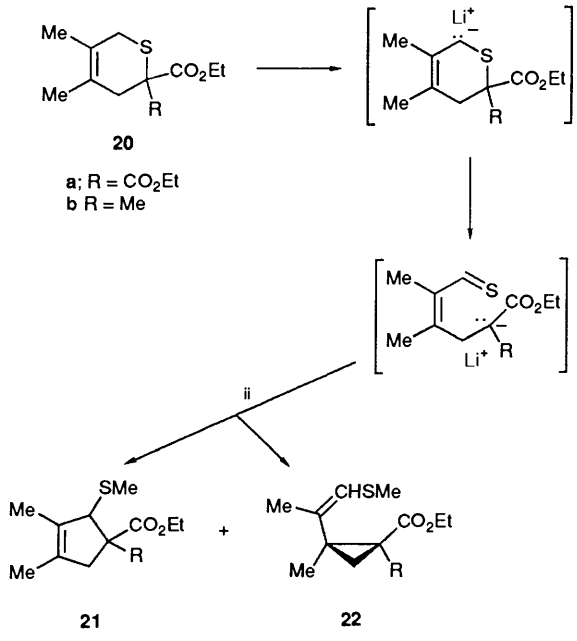
Methylation of the dilithio derivatives **9d**, **13d** and **4b** (Li replacing Et) was also briefly studied. Lithiation of the corresponding carboxylic acids was effected, in the usual way, in THF with LDA (*ca.* 2.5 mol equiv.). When the bicyclic dilithio derivatives **9d** and **13d** were treated with methyl iodide, they underwent rearrangement and *S*-methylation, in the manner observed for the corresponding monolithio esters, to give the cyclopropanecarboxylic acids **10b** and **14b**, respectively. Again, the dilithiothiine **4b** (Li replacing Et) underwent *C*-methylation, like the monolithio ester **4b**, to give the 2-methyl carboxylic acid **4c** (H replacing Et). Even when this monocyclic dilithio derivative was kept at room temperature for several hours, in the absence of methyl iodide, no rearrangement to a cyclopropanecarboxylic acid (like **19**) occurred; acidification of the mixture regenerated the thiinecarboxylic acid **4a** (H replacing Et) in good yield. However, the carbanions derived from the corresponding sulphonium salts **17a–b** (Scheme 5)




**Scheme 5** *Reagents:* i, (a) $Me_3OBF_4$ or (b) $Et_3OBF_4$ in $CH_2Cl_2$ at 20 °C for 2 h; ii, diazabicyclononene in MeCN at 0 °C for 20 min

rearranged rapidly. Thus, the cycloadduct **4a** was treated with either trimethyl- or triethyl-oxonium tetrafluoroborate at room temperature to afford the sulphonium salts **17a** and **17b**. These were converted cleanly into the cyclopropanecarboxylates **19a** and **19b** upon treatment with diazabicyclononene.* Again, the products were formed stereospecifically, as expected from concerted rearrangements, of the familiar type **18**→**19**, of the sulphur ylides **18**.

The foregoing rearrangements provide efficient, 'one-pot' routes for the conversion of thioaldehyde cycloadducts into substituted, functionalised cyclopropanes.† A synthetically valuable, complementary set of carbanion rearrangements, to form cyclopentenes and cyclopropenes, has been reported by Larsen[3] for the monocyclic cycloadducts of diethyl thioxomalonate, which was prepared from the corresponding Bunte salt[3,5] and trapped *in situ* by a wide range of dienes (Scheme 6).




**Scheme 6** *Reagents:* i, LDA and HMPA in THF, or $KN(SiMe_3)_2$ in THF or $Et_2O$; ii, MeI

For example, the cycloadduct **20a** gave, by successive treatment with LDA and methyl iodide, the cyclopentene **21a**. In an isolated example, the cycloadduct **20b** (*i.e.* **4c**) of the methyl thioketone **2c** also underwent rearrangement and methylation to afford both cyclopentene **21b** and cyclopropane **22b** derivatives. The conversion of thioketone cycloadducts into cyclopropane derivatives of the type **22** was reported earlier by Biellmann and Ducep.[6]

## Experimental

*General Methods.*—Mass spectra were obtained by electron impact at 70 eV. TLC was carried out on Merck silica gel 60 $GF_{254}$ plates, and compounds were located by UV light or iodine vapour. Column chromatography employed TLC-grade silica, with reduced pressure to assist flow.[7] Extracts in organic solvents were dried over $MgSO_4$ and evaporated in a Buchi Rotavapor. *J* Values are given in Hz.

*C-Alkylation of the Cycloadducts of Dimethylbutadiene* **4a** *and Anthracene* **1a**.—Generally, the cycloadducts in tetrahydrofuran (THF) were treated successively with approximately equimolecular amounts of lithium diisopropylamide (LDA) and the appropriate 'alkyl' (allyl, benzyl, ethyl or methyl) halide. Alkylation was allowed to proceed for several hours at room temperature. Occasionally, a moderate excess of LDA and the alkyl halide was employed, but not for benzylation since competitive attack of LDA on benzyl bromide occurred. Typical conditions and work-up are exemplified for allylation of the dimethylbutadiene adduct **4a** and benzylation of the anthracene adduct **1a** as follows.

The 12-substituted anthracene derivatives **1c–f** showed two general spectroscopic features of special note. Their mass spectra all showed weak molecular ion peaks, and base peaks, *m/z* 178, corresponding to an anthracene cation radical

* Thermolysis (FVP at 400 °C and $10^{-2}$ mbar) of the cyclopropane derivative **19a** caused efficient rearrangement, as expected,[4] to yield the symmetrical isomer, ethyl 3,4-dimethyl-1-methylthiocyclopent-3-ene-1-carboxylate.

† The methyl esters of the acids **10b**, **14b** and **19a** (H replacing Et) were prepared earlier[4] by an alternative route involving cationic cycloadditions.

($C_{14}H_{10}$). The IR spectra, for solutions in $CCl_4$, showed two strong, carbonyl bands, average frequencies $\nu$ 1734 and 1717 $cm^{-1}$, except for that of the 12-methyl derivative **1c** which showed one, broad band, $\nu$ 1729 $cm^{-1}$.

*Ethyl 2-Allyl-3,6-dihydro-4,5-dimethyl-2H-thiine-2-carboxylate* **4e**.—Butyllithium (1.6 mol $dm^{-3}$ solution in hexanes; 5 mmol) was added with stirring to diisopropylamine (5 mmol) in THF (20 $cm^3$) at −78 °C (notional bath temperature; acetone–solid carbon dioxide) under dry nitrogen. After 20 min the cycloadduct[1] **4a** (1.0 g, 5 mmol) was added, and the mixture was stirred for 1 h. Allyl bromide (0.80 g, 6.6 mmol) was then added and the mixture was allowed to warm up to 20 °C during 0.5 h; stirring was continued for 3 h at 20 °C. The mixture was evaporated and the residue was agitated with dichloromethane and 5% hydrochloric acid. The dichloromethane layer was washed with water, dried, and evaporated. Distillation (Kugelrohr, *ca.* 170 °C, *ca.* 0.3 mmHg) of the residue gave the *2-allyl derivative* **4e** (0.92 g, 77%) as an oil (Found: M, 240.1190. $C_{13}H_{20}O_2S$ requires *M*, 240.1184); $\nu_{max}(CCl_4)/cm^{-1}$ 1729; $\delta_H$(200 MHz; $CDCl_3$) 1.19 (t, *J* 7.1, $OCH_2Me$), 1.64 (br s, 4- and 5-Me), 2.21 and 2.53 (br ABq, *J* 17, 3- or 6-$CH_2$), 2.43 (ddt, *J* 13.9, 7.5 and 1.1, $CH_2$=CHC$H_2$), 2.55 (ddt, *J* 13.9, 7.1 and 1.1, $CH_2$=CHC$H_2$), 2.85 and 3.14 (br ABq, *J* 17, 6- or 3-$CH_2$), 4.11 (q with fine splitting, *J* 7.1, OC$H_2$Me), 5.01 and 5.08 [2 × m, $\delta_A \simeq \delta_B \simeq$ 5.04(5), C$H_AH_B$=CH] and 5.61–5.82 (m, $CH_2$=C*H*$CH_2$); $\delta_C$(50.3 MHz; $CDCl_3$) 14.1 ($OCH_2Me$), 19.0 (4- or 5-Me), 20.2 (5- or 4-Me), 30.6 ($CH_2$=CH*C*$H_2$), 39.9 (C-3 or -6), 42.7 (C-6 or -3), 50.6 (C-2), 61.1 (O*C*$H_2$Me), 118.6 (*C*$H_2$=CH), 122.2 (C-4 or -5), 125.9 (C-5 or -4), 132.4 ($CH_2$=*C*H) and 172.7 (C=O).

*Ethyl 3,6-Dihydro-2,4,5-trimethyl-2H-thiine-2-carboxylate* **4c**.[3] Alkylation, as before but with methyl iodide, gave, after Kugelrohr distillation, the 2-methyl derivative **4c** as an oil (78%) (Found: M, 214.1028. Calc. for $C_{11}H_{18}O_2S$: *M*, 214.1027); $\nu_{max}(CCl_4)/cm^{-1}$ 1726; $\delta_H$(200 MHz; $CDCl_3$) 1.19 (t, *J* 7.1, $OCH_2Me$), 1.44 (s, 2-Me), 1.63 and 1.65 (2 × br s, 4- and 5-Me), 2.16 and 2.56 (br ABq, *J* 17, 3- or 6-$CH_2$), 2.85 and 3.17 (br ABq, *J* 17, 6- or 3-$CH_2$) and 4.10 (q with fine splitting, *J* 7.1, OC$H_2$Me); $\delta_C$(50.3 MHz; $CDCl_3$) 14.0 ($OCH_2Me$), 19.0 (2-Me), 20.2 (4- or 5-Me), 25.4 (5- or 4-Me), 30.9 (C-3 or -6), 42.2 (C-6 or -3), 46.2 (C-2), 61.1 (O*C*$H_2$Me), 121.8 (C-4 or -5), 126.0 (C-5 or -4) and 173.8 (C=O). The $^1H$ NMR, IR, and MS (apart from the relative intensities of fragment ion peaks) data agreed well with those in the Supplementary Material of ref. 3.

3,6-*Dihydro-2,4,5-trimethyl-2H-thiine-2-carboxylic Acid* (**4c**; H *replacing* Et). The foregoing ethyl ester **4c** (1 mmol) was kept in ethanol (10 $cm^3$) and aqueous sodium hydroxide (1 mol $dm^{-3}$; 10 $cm^3$) at room temperature overnight. The mixture was evaporated and the residue was dissolved in water. Neutral impurities were extracted with dichloromethane and, after acidification of the aqueous solution, the acidic product was, in turn, extracted with dichloromethane. The *2-methyl carboxylic acid* **4c** (H replacing Et) was obtained as crystals (80%), m.p. 93–94 °C [from light petroleum (b.p. 40–60 °C)] (Found: C, 58.2; H, 7.6%; M, 186.0717. $C_9H_{14}O_2S$ requires C, 58.0; H, 7.6%; *M*, 186.0715); $\nu_{max}(CCl_4)/cm^{-1}$ 1702, with broad absorption in the region 2300–3500; $\delta_H$(200 MHz; $CDCl_3$) 1.53 (s, 2-Me), 1.67 (br s, 4- or 5-Me), 1.71 (br s, 5- or 4-Me), 2.23 and 2.61 (br ABq, *J* 17, 3- or 6-$CH_2$), 2.90 and 3.31 (br ABq, *J* 17, 6- or 3-$CH_2$) and 10.9 (br s, OH, exch. with $D_2O$); $\delta_C$(50.3 MHz; $CDCl_3$) 19.2 (2-Me), 20.25 (4- or 5-Me), 25.8 (5- or 4-Me), 31.0 (C-3 or -6), 41.8 (C-6 or -3), 46.3 (C-2), 122.1 (C-4 or -5), 126.0 (C-5 or -4) and 180.2 (C=O).

*Ethyl 2-Ethyl-3,6-dihydro-4,5-dimethyl-2H-thiine-2-carboxylate* **4d**. Prepared similarly but with ethyl iodide, the *2-ethyl derivative* **4d** was obtained after Kugelrohr distillation as an oil (72%) (Found: C, 62.9; H, 8.6%; M, 228.1179. $C_{12}H_{20}O_2S$ requires C, 63.1; H, 8.8%; *M*, 228.1183); $\nu_{max}(CCl_4)/cm^{-1}$ 1727; $\delta_H$(200 MHz; $CDCl_3$) 0.80 [t, *J* 7.5, C(2)$CH_2Me$], 1.11 (t, *J* 7.1, $OCH_2Me$), 1.55 (br s, 4- and 5-Me), 1.64 and 1.74 [qABq, $J_{gem}$ 13.8 and $J_{vic}$ 7.7, C(2)C$H_2$Me], 2.10 and 2.47 (br ABq, *J* 17, 3- or 6-$CH_2$), 2.73 and 3.05 (br ABq, *J* 17, 6- or 3-$CH_2$) and 4.01 and 4.04 (qABq, $J_{gem}$ 10.6 and $J_{vic}$ 7.1, OC$H_2$Me); $\delta_C$(50.3 MHz; $CDCl_3$) 8.8 [C(2)$CH_2Me$], 13.9 ($OCH_2Me$), 18.8 (4- or 5-Me), 20.0 (5- or 4-Me), 30.4 [C(2)*C*$H_2$Me], 31.3 (C-3 or -6), 40.1 (C-6 or -3), 51.4 (C-2), 60.7 (O*C*$H_2$Me), 121.9 (C-4 or -5), 125.7 (C-5 or -4) and 172.8 (C=O).

*Ethyl 2-Benzyl-3,6-dihydro-4,5-dimethyl-2H-thiine-2-carboxylate* **4f**. Prepared like the allyl derivative **4e** but with benzyl bromide in place of allyl bromide, the *2-benzyl derivative* **4f** was obtained, after Kugelrohr distillation (150–170 °C, 0.3 mmHg), as a syrup (78%) (Found: C, 70.1; H, 7.5%; M, 290.1337. $C_{17}H_{22}O_2S$ requires C, 70.3; H, 7.6%; *M*, 290.1340); $\nu_{max}(CCl_4)/cm^{-1}$ 1728; $\delta_H$(200 MHz; $CDCl_3$) 1.20 (t, *J* 7.1, $OCH_2Me$), 1.67 (br s, 4- and 5-Me), 2.32 and 2.54 (br ABq, *J* 17, 3- or 6-$CH_2$), 2.96 and 3.20 (br ABq, *J* 17, 6- or 3-$CH_2$), 3.04 and 3.22 (ABq, *J* 13.5, PhC$H_2$), 4.11 (q, *J* 7.1, OC$H_2$Me) and 7.12–7.30 (m, Ph); $\delta_C$(50.3 MHz; $CDCl_3$) 14.05 ($OCH_2Me$), 19.1 (4- or 5-Me), 20.35 (5- or 4-Me), 31.0 (Ph*C*$H_2$), 40.1 (C-3 or -6), 44.4 (C-6 or -3), 52.0 (C-2), 61.25 (O*C*$H_2$Me), 122.0 (C-4 or -5), 126.1 (C-5 or -4), 127.0, 128.1 and 129.9 (*o*-, *m*- and *p*-phenyl-CH), 135.9 (*ipso*-phenyl-C) and 172.75 (C=O).

*Ethyl 12-Benzyl-9,10-dihydro-10,9-(epithiomethano)anthracene-12-carboxylate* **1f**. LDA (5 mmol) was prepared from butyllithium and diisopropylamine in THF at −20 °C, as described in the foregoing preparation of the 2-allyldihydrothiine **4e**. The mixture was allowed to warm up to 0 °C. The anthracene cycloadduct[1] **1a** (1.48 g, 5 mmol) was then added and the mixture was stirred and allowed to warm up to 20 °C. The mixture was cooled to −20 °C, then benzyl bromide (6 mmol) was added with stirring. Stirring was continued at −20 °C for 1 h and then at 20 °C for 3 h. After the usual work-up, the product was purified by preparative TLC on silica plates developed with hexane–ethyl acetate (3:2). The *12-benzyl derivative* **1f** (1.56 g, 81%) had m.p. 124 °C [from light petroleum (b.p. 40–60 °C)] (Found: C, 77.8; H, 5.65%; M, 386.1338. $C_{25}H_{22}O_2S$ requires C, 77.7; H, 5.7%; *M*, 386.1341); $\nu_{max}(CCl_4)/cm^{-1}$ 1737 and 1714; $\delta_H$(200 MHz; $CDCl_3$) 0.98 (t, *J* 7.1, Me), 2.75 and 3.30 (ABq, *J* 13.4, PhC$H_2$), 3.88 (q, *J* 7.1, OC$H_2$Me), 4.97 (s, 9- or 10-H), 5.08 (s, 10- or 9-H) and 7.02–7.52 (13 H, m, ArH); $\delta_C$(50.3 MHz; $CDCl_3$) 13.8 (Me), 46.4 (C-9 or -10), 46.7 (Ph$CH_2$), 53.15 (C-10 or -9), 61.4 (O*C*$H_2$Me), 67.7 (C-12), 122.0, 122.05, 125.8, 126.5, 126.6, 126.9, 127.1, 127.2, 127.25, 128.0 and 129.7 (ArCH), and 136.46, 139.1, 139.9, 143.2 and 143.3 (ArC) and 172.5 (C=O).

*Ethyl 9,10-Dihydro-12-methyl-10,9-(epithiomethano)anthracene-12-carboxylate* **1c**. Alkylation as before, but with methyl iodide, gave the *12-methyl derivative* **1c** (87%) as thick plates [from dichloromethane–light petroleum (b.p. 40–60 °C)] (Found: C, 73.5; H, 5.8% M, 310.1019. $C_{19}H_{18}O_2S$ requires C, 73.5; H, 5.8%; *M*, 310.1028); $\nu_{max}(CCl_4)/cm^{-1}$ 1729; $\delta_H$(90 MHz; $CDCl_3$) 1.14 (t, *J* 7, $OCH_2Me$), 1.41 (s, 12-Me), 4.02 (br q, *J* 7, OC$H_2$Me), 4.76 (s, 9- or 10-H), 5.03 (s, 10- or 9-H) and 7.1–7.5 (m, ArH).

*Ethyl 12-Ethyl-9,10-dihydro-10,9-(epithiomethano)anthracene-12-carboxylate* **1d**. Alkylation as before, but with ethyl iodide, gave the *12-ethyl derivative* **1d** (83%) as crystals, m.p. 104 °C [from light petroleum (b.p. 40–60 °C)] (Found: C, 74.3; H, 6.5%; M, 324.1186. $C_{20}H_{20}O_2S$ requires C, 74.1; H, 6.2%; *M*, 324.1184); $\nu_{max}(CCl_4)/cm^{-1}$ 1731 and 1718; $\delta_H$(90 MHz; $CDCl_3$) 0.84 [t, *J* 7, C(12)$CH_2Me$)], 1.11 (t, *J* 7, $OCH_2Me$), 1.1–2.1 [2 H, m, C(12)C$H_2$Me], 4.03 (q, *J* 7, OC$H_2$Me), 4.86 (s, 9- or 10-H), 5.00 (s, 10- or 9-H) and 7.0–7.5 (m, ArH).

*Ethyl 12-Allyl-9,10-dihydro-10,9-(epithiomethano)anthracene-12-carboxylate* **1e**. Alkylation as before, but with allyl

bromide, gave the 12-*allyl derivative* **1e** (87%), which formed crystals, m.p. 96 °C [from light petroleum (b.p. 40–60 °C)] (Found: C, 75.0; H, 5.9%; M, 336.1154. $C_{21}H_{20}O_2S$ requires C, 75.0; H, 6.0%; *M*, 336.1183); $\nu_{max}(CCl_4)/cm^{-1}$ 1733 and 1719; $\delta_H$(200 MHz; $CDCl_3$) 1.16 (t, *J* 7.1, $OCH_2Me$), 2.30 (ddt, *J* 13.9, 6.5 and 1.3, $CH_2$=CHC$H_2$), 2.48 (br dd, *J* 13.9 and 7.8, $CH_2$=CHC$H_2$), 3.99 and 4.07 (qABq, $J_{gem}$ 10.8 and $J_{vic}$ 7.1, OC$H_2$Me), 4.91 (s, 9- or 10-H), 5.06 (s, 10- or 9-H), 5.06 (dm, *J ca.* 16, C$H_2$=CH), 5.10 (dm, *J ca.* 10, C$H_2$=CH), 5.73 (dddd, *J* 16.5, 10.4, 7.8 and 6.5, $CH_2$=C*H*) and 7.05–7.45 (m, ArH); $\delta_C$(50.3 MHz; $CDCl_3$) 14.1 (Me), 45.4 ($CH_2$=CHC$H_2$), 46.4 (C-9 or -10), 51.5 (C-10 or -9), 61.5 ($OCH_2$), 65.2 (12-C), 118.8 (C$H_2$=CH), 121.8, 122.0, 125.8, 126.5, 126.8, 126.85 and 127.0 (ArCH), 132.8 ($CH_2$=CH), 139.1, 139.9, 142.7 and 143.3 (ArC) and 172.2 (C=O).

*Preparation of the Cycloadducts* **4–8** *by Retro-Diels–Alder Cleavage of the Anthracene Adducts* **1c–f**.—Generally, the appropriate anthracene adduct (0.5 mmol) was heated with either 2,3-dimethylbuta-1,3-diene (DMB), cyclopentadiene, or cyclohexa-1,3-diene (typically 2.5 mmol) in toluene (5 $cm^3$) under reflux, under nitrogen, until 'transfer' of the thioketone **2** was complete (TLC control) (typically 5 h). The mixture was evaporated and the residue was triturated with methanol and set aside to allow anthracene to crystallise out. The mixture was filtered and the filtrate was evaporated. The residue was shown in each case, by $^1H$ NMR spectroscopy, to contain the corresponding adduct(s) **4–8** of the diene and, usually, traces of anthracene. No other products were detected. The products (yields *ca.* 90%) were further purified by chromatography or Kugelrohr distillation.

The DMB adducts **4c–f** were identified by comparison of their $^1H$ NMR spectra with those of samples prepared, as described before, from **4a**. The oily cyclopentadiene adducts **5** and **6** were separated by chromatography on a silica gel column. Elution with hexane gave a trace of anthracene, then hexane–ethyl acetate (98:2) gave, successively, *ethyl 3-methyl-2-thiabicyclo*[2.2.1]*hept-5-ene*-3-exo-*carboxylate* **5** (60% yield from **1c**) (Found: C, 60.6; H, 7.1%; M, 198.0698. $C_{10}H_{14}O_2S$ requires C, 60.6; H, 7.1%; *M*, 198.0714); $\nu_{max}(CCl_4)/cm^{-1}$ 1728; $\delta_H$(200 MHz; $CDCl_3$) 1.26 (t, *J* 7.1, $OCH_2Me$), 1.38 (s, 3-Me), 1.78 (dt, *J* 9.5 and 2.3, 7-H), 1.90 (dm, *J* 9.5, 7-H), 3.48 (m, 4-H), 3.98 (m, 1-H), 4.19 (q, *J* 7.1, with fine splitting, OC$H_2$Me), 5.97 (dd, *J* 5.5 and 3.3, 5- or 6-H), and 6.42 (dd, *J* 5.3 and 2.8, 6- or 5-H); $\delta_C$(50.3 MHz; $CDCl_3$) 14.1 ($OCH_2Me$), 23.8 (3-Me), 52.3 (C-1 or -4), 52.4 (C-7), 52.9 (C-4 or -1), 61.0 (C-3), 61.3 (OC$H_2$Me), 131.8 (C-5 or -6), 138.7 (C-6 or -5) and 175.4 (C=O); then *ethyl 3-methyl-2-thiabicyclo*[2.2.1]*hept-5-ene*-3-endo-*carboxylate* **6** (20%) (Found: C, 60.5; H, 7.1%; M, 198.0702. $C_{10}H_{14}O_2S$ requires C, 60.6; H, 7.1%; *M*, 198.0714); $\nu_{max}(CCl_4)/cm^{-1}$ 1730; $\delta_H$(200 MHz; $CDCl_3$) 1.22 (t, *J* 7.1, $OCH_2Me$), 1.73 (dt, *J* 9.4 and 2, 7-H), 1.82 (s, 3-Me), 1.89 (dm, *J ca.* 9, 7-H), 3.26 (m, 4-H), 4.00 (m, 1-H), 4.12 (q, *J* 7.1, with fine splitting, OC$H_2$Me), 6.01 (dd, *J* 5.2 and 3.1, 5- or 6-H) and 6.40 (dd, *J* 5.4 and 2.8, 6- or 5-H); $\delta_C$(50.3 MHz; $CDCl_3$) 14.1 ($OCH_2Me$), 28.3 (3-Me), 49.4 (C-7), 52.9 (C-1 or -4), 54.0 (C-4 or -1), 61.2 (OC$H_2$Me), 63.7 (C-3), 134.0 (C-5 or -6), 138.3 (C-6 or -5) and 174.3 (C=O).

The oily cyclohexadiene adducts **7** and **8** could not be separated, and consequently were characterised as a mixture: *ethyl 3-methyl-2-thiabicyclo*[2.2.2]*oct-5-ene*-3-exo-*carboxylate* **7** and 3-endo-*carboxylate* **8** (**7**:**8** = *ca.* 1:1) (Found: M, 212.0865. $C_{11}H_{16}O_2S$ requires *M*, 212.0871); $\nu_{max}(CCl_4)/cm^{-1}$ 1727; $\delta_H$(200 MHz; $CDCl_3$) 1.21 and 1.27 (2 × t, *J* 7.1, 2 × $OCH_2Me$), 1.37 and 1.71 (2 × s, 3-Me in **7** and **8**, respectively), 1.52–2.11 (m, 7- and 8-$CH_2$), 3.03 (t, *J* 5.5, with fine splitting, 1-or 4-H), 3.11 (t, *J* 5.8, with fine splitting, 1- or 4-H), 3.45 (m, 4- or 1-H, in both **7** and **8**), 3.97–4.31 (2 × m, 2 × OC$H_2$Me), 6.24 and 6.50 (2 × t, *J* 7.8, with fine splitting, 5- and 6-H) and 6.36 and 6.47 (2 × t, *J* 7.5, with fine splitting, 5- and 6-H); $\delta_C$(50.3 MHz; $CDCl_3$) 14.0 and 14.1 ($OCH_2Me$), 18.4, 20.6, 28.1 and 29.0 (C-7 and -8), 25.6 and 28.8 (3-Me), 36.0, 36.2, 37.5 and 37.7 (C-1 and -4), 57.1 and 58.1 (C-3), 61.1 and 61.4 (OC$H_2$Me), 131.4, 133.7, 134.3 and 134.8 (C-5 and -6) and 174.8 and 175.2 (C=O).

*Retro-Diels–Alder Cleavage of the Cyclopentadiene Cycloadduct* **5**.—The cycloadduct **5** (100 mg, 0.505 mmol) and 2,3-dimethylbutadiene (DMB) (124 mg, 1.515 mmol) were heated in toluene (7 $cm^3$) under reflux, under nitrogen, for 4 h. The mixture was evaporated to afford the DMB adduct **4c** (80 mg), which was identified by $^1H$ NMR spectroscopy (90 MHz) and found to contain no significant amounts of the cycloadducts **5** or **6**, or any byproduct. When a mixture of the cycloadducts **5** or **6** (*ca.* 3:1) was heated as before, but in the absence of DMB, slow decomposition was observed ($^1H$ NMR control). After 5 h, signals for the cycloadducts **5** and **6** (*ca.* 2:1) were accompanied by broad signals arising perhaps from a thioketone polymer. After 20 h, decomposition was complete.

*Rearrangement and Methylation of the Lithio Derivative* **9b** *of the Cyclopentadiene Adducts* **9a**.—An *endo–exo* mixture[2] of the cyclopentadiene adducts **9a** (2.45 mmol) was treated in THF with LDA (3 mmol) at −78 °C and then with methyl iodide (2.7 mmol) at 10 °C, as described for the alkylation of the cycloadducts **1a** and **4a**. After the mixture had been kept at room temperature for 2 h, work-up gave *ethyl* (1S*,5R*,6R*)-6-*methylthiobicyclo*[3.1.0]*hex-2-ene-6-carboxylate* **10a** (89%) as an oil (Found: M, 198.0714. $C_{10}H_{14}O_2S$ requires *M*, 198.0714); $\nu_{max}(CCl_4)/cm^{-1}$ 1729 and 1712; $\delta_H$(200 MHz; $CDCl_3$) 1.26 (t, *J* 7.1, $OCH_2Me$), 1.97 (s, SMe), 2.28 (dq, *J* 18.5 and *ca.* 2, 4-H), 2.48 (t, *J* 6.7, 5-H), 2.61 (ddt, *J* 18.5, 6.6, and *ca.* 2, 4-H), 2.76 (dt, *J* 6.7 and *ca.* 2, 1-H), 4.15 (q, *J* 7.1, OC$H_2$Me), 5.72 (dq, *J* 5.5 and *ca.* 2, 2- or 3-H) and 5.81 (dm, *J* 5.5, 3- or 2-H) (all signals except those at $\delta$ 1.26 and 1.97 showed additional fine splitting); $\delta_C$(50.3 MHz; $CDCl_3$) 14.2 ($OCH_2Me$), 16.6 (SMe), 33.8 (C-1 or -5), 34.3 (C-4), 38.0 (C-6), 43.1 (C-5 or -1), 61.5 (OC$H_2$Me), 126.0 and 135.9 (C-2 and -3) and 173.0 (C=O).

For further characterisation, the ester **10a** (260 mg) was hydrolysed in ethanol (15 $cm^3$) and sodium hydroxide (1 mol $dm^{-3}$; 15 $cm^3$) at room temperature for 24 h to afford the corresponding *carboxylic acid* **10b** (200 mg, 90%) as plates, m.p. 104–105 °C [from light petroleum (b.p. 40–60 °C)] (Found: C, 56.3; H, 5.95%; M, 170.0390. $C_8H_{10}O_2S$ requires C, 56.5; H, 5.9%; *M*, 170.0401); $\nu_{max}(CCl_4)/cm^{-1}$ 2300–3400 (br) and 1685; $\delta_H$(200 MHz; $CDCl_3$) 1.99 (s, SMe), 2.31 (dq, *J* 18 and 2, 4-H), 2.56 (br t, *J* 6.5, 5-H), 2.65 (ddt, *J* 18, 6.6 and 1.9, 4-H), 2.89 (dt, *J* 6.5 and *ca.* 2, 1-H), 5.76 (dq, *J* 5.5 and 1.6, 2- and 3-H), 5.85 (m, 3-or 2-H) and 12.27 (br s, OH, exch. with $D_2O$); $\delta_C$(50.3 MHz; $CDCl_3$) 16.5 (SMe), 34.5 (C-4), 35.0 (C-1 or -5), 38.2 (C-6), 44.1 (C-5 or -1), 125.9 (C-2 or -3), 136.25 (C-3 or -2) and 179.2 (C=O).

*Rearrangement and Methylation of the Lithio Derivative* **13b** *of the Cyclohexadiene Adducts* **13a**.—An *endo–exo* mixture (largely *endo*) of the cyclohexadiene adducts[1] **13a** (2.52 mmol) was treated in THF at −78 °C with LDA (3.0 mmol), as described for the alkylation of the cycloadducts **1a** and **4a**. The mixture was warmed up to −40 °C, then methyl iodide (3.0 mmol) was added. After the mixture had been kept at room temperature for 2 h, work-up gave *ethyl* (1S*,2R*,7R*)-7-*methylthiobicyclo*[4.1.0]*hept-2-ene-7-carboxylate* **14a** (61%) as an oil (Found: M, 212.0880. $C_{11}H_{16}O_2S$ requires *M*, 212.0871); $\nu_{max}(CCl_4)/cm^{-1}$ 1705; $\delta_H$(200 MHz; $CDCl_3$) 1.22 (t, *J* 7.1, $OCH_2Me$), 1.81–1.92 (2 H, m), 1.92–2.16 (4 H, m), 2.05 (s, SMe),

4.11 (q, *J* 7.1, $OCH_2Me$), 5.76 (dm, *J* 9.9, 2- or 3-H) and 5.83 (dt, *J* 9.9 and 3.5, 3- or 2-H); $\delta_C$(50.3 MHz; $CDCl_3$) 14.1 ($OCH_2Me$), 16.2 (C-4 or -5), 16.3 (SMe), 21.7 (C-5 or -4), 27.3 and 27.5 (C-1 and -6), 42.4 (C-7), 61.4 ($OCH_2$), 120.3 (C-2 or -3), 130.7 (C-3 or -2) and 172.2 (C=O).

Hydrolysis of this ester **14a**, as described for the foregoing ester **10a**, gave the corresponding *carboxylic acid* **14b** as plates, m.p. 110–111 °C (from diethyl ether) (Found: C, 58.6; H, 6.6%; M, 184.0554. $C_9H_{12}O_2S$ requires C, 58.7; H, 6.6%; *M*, 184.0558); $\nu_{max}(CCl_4)/cm^{-1}$ 1740 (weak) and 1687 (strong); $\delta_H$(200 MHz; $CDCl_3$) 1.87–2.36 (6 H, m), 2.11 (s, SMe), 5.81 (dm, *J* 10.0, 2- or 3-H), 5.90 (dt, *J* 10.0 and 3.6, 3- or 2-H) and *ca.* 12 (br s, OH); $\delta_C$(50.3 MHz; $CDCl_3$) 16.3 (C-4 or -5), 16.4 (SMe), 21.7 (C-5 or -4), 28.5 and 28.8 (C-1 and -6), 42.6 (C-7), 120.1 (C-2 and -3), 131.2 (C-3 or -2) and 178.1 (C=O).

*Acid-catalysed Rearrangements of the Cyclopropanecarboxylic Acid* **14b** *to give the Lactones* **15** *and* **16**.—The foregoing acid **14b** decomposed slowly, when stored at room temperature in the crystalline state, to give a mixture of the lactones **15** and **16** (ratio *ca.* 1:1). This rearrangement was effected with acid catalysis as follows. The acid **14b** (80 mg) was heated in chloroform (7 $cm^3$) under reflux with a catalytic amount of hydrochloric acid until the reaction was complete (TLC control). The mixture was evaporated and the residue was chromatographed on a short column of silica gel. Elution with hexane–ethyl acetate (1:1) gave a mixture (48 mg) of the lactones **15** and **16** (ratio *ca.* 1:2). Rechromatography on silica gel and elution with hexane–diethyl ether (1:1) gave successively (1R*,6S*,9S*)-9-*methylthio*-7-*oxabicyclo*[4.3.0]*non*-4-*en*-8-*one* **15** (32 mg), as an oil (Found: M, 184.0556. $C_9H_{12}O_2S$ requires *M*, 184.0558); $\nu_{max}(CCl_4)/cm^{-1}$ 1762; $\delta_H$(200 MHz; $CDCl_3$) 1.56 (dddd, *J* 13.4, 10.5, 8.3 and 5.8, 2-H), 1.81 (dq, *J* 13.4 and 4.8, 2-H), 1.91–2.28 (m, 3-$H_2$), 2.27 (s, SMe), 2.37 (ddt, *J* 10.5, 6.0 and 4.3, 1-H), 3.19 (d, *J* 3.9, 9-H), 4.94 (br t, *J ca.* 5, 6-H), 5.86 (ddtd, *J* 10.0, 3.8, 2.0 and 0.5, 5-H) and 6.11 (ddddd, *J* 10.0, 4.7, 3.1, 1.0 and 0.5, 4-H); $\delta_C$(50.3 MHz; $CDCl_3$) 14.4 (Me), 22.6 and 22.8 (C-2 and -3), 40.5 (C-1), 47.2 (C-9), 74.0 (C-6), 122.7 (C-4 or -5), 134.1 (C-5 or -4) and 174.1 (C-8); then (1R*,6S*,9R*)-9-*methylthio*-7-*oxabicyclo*[4.3.0]*non*-4-*ene*-8-*one* **16** (15 mg) as needles, m.p. 75–76 °C [from light petroleum (b.p. 40–60 °C)] (Found: C, 58.6; H, 6.6%; M, 184.0547. $C_9H_{12}O_2S$ requires C, 58.7; H, 6.6%; *M*, 184.0558); $\nu_{max}(CCl_4)/cm^{-1}$ 1764; $\delta_H$(200 MHz; $CDCl_3$) 1.13–1.36 (m, 2-$H_2$), 1.80–2.30 (m, 3-$H_2$), 2.30 (s, SMe), 2.64 (tdd, *J* 9.3, 7.4 and 4.7, 1-H), 3.84 (d, *J* 7.3, 9-H), 4.67 (t, *J* 4.6, with fine splitting, 6-H), 5.93 (dddd, *J* 10.0, 4.0, 2.5 and 1.5, 5-H) and 6.20 (dddt, *J* 10.0, 5.6, *ca.* 2, and *ca.* 1, 4-H); $\delta_C$(50.3 MHz; $CDCl_3$) 15.5 (Me), 19.8 (C-2 or -3), 23.8 (C-3 or -2), 38.7 (C-1), 50.8 (C-9), 73.4 (C-6), 122.0 (C-4 or -5), 135.8 (C-5 or -4) and 174.7 (C-8).

*Methylation of the Dilithio Derivatives* **9d**, **13d** *and* **4b** (Li *replacing* Et).—In general, in separate experiments, the carboxylic acids[1,2] **9c**, **13c** and **4a** (H replacing Et) (2 mmol) were added to LDA (5 mmol), prepared at −78 °C in THF (10 $cm^3$) as described for the alkylation of the esters **1a** and **4a**. Methyl iodide (2.4 mmol) was added at 0 °C, and the mixtures were kept at 0 °C for 1 h. Work-up gave (*ca.* 80% yield) the cyclopropanecarboxylic acids **10b** and **14b**, and the thiinecarboxylic acid **4c** (H replacing Et), respectively. These products were identified by spectroscopic comparison with samples prepared by hydrolysis of the corresponding esters, as described before.

*Ethyl* (1S*,2S*)-*Isoprop*-2-*enyl*-2-*methyl*-1-*methylthiocyclopropane*-1-*carboxylate* **19a** *and the Corresponding Ethylthio Derivative* **19b**.—The thiinecarboxylate[1] **4a** (550 mg, 2.75 mmol) and trimethyloxonium tetrafluoroborate (440 mg, 2.98 mmol) were stirred in dry dichloromethane (20 $cm^3$) at room temperature for 2 h. The mixture was evaporated and the residue was dissolved in dry acetonitrile (5 $cm^3$) with stirring under nitrogen at 0 °C. 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) (390 mg, 3.14 mmol) was added dropwise to the mixture, and stirring was continued for 20 min. Water (20 $cm^3$) was added, and the mixture was extracted with diethyl ether (3 × 30 $cm^3$). The extracts were washed successively with dilute hydrochloric acid and brine, then were dried and evaporated. Distillation (Kugelrohr, 140–165 °C, 0.3 mmHg) of the residue gave the *cyclopropanecarboxylate* **19a** as an oil (480 mg, 82%) (Found: M, 214.1039. $C_{11}H_{18}O_2S$ requires *M*, 214.1028); $\nu_{max}/cm^{-1}$ 1720; $\delta_H$(200 MHz; $CDCl_3$) 1.20 (s, 2-Me), 1.27 (t, *J* 7.1, $OCH_2Me$), 1.28 and 1.63 (ABq, *J* 5.1, 3-$H_2$), 1.79 (dd, *J* 1.4 and 0.8, vinyl-Me), 2.07 (s, SMe), 4.19 (q, *J* 7.1, with fine splitting, $OCH_2Me$), 4.83 (quintet, *J* 0.8, C=$CH_2$) and 4.91 (quintet, *J* 1.5, C=$CH_2$); $\delta_C$(50.3 MHz; $CDCl_3$) 14.3, 15.7, 20.1, and 21.1 (4 × Me), 27.0 (C-3), 38.36 and 38.39 (C-1 and -2), 61.3 ($OCH_2Me$), 113.4 (C=$CH_2$), 145.6 (*C*=$CH_2$) and 171.2 (C=O).

This preparation was repeated, but with triethyl, rather than trimethyl, oxonium fluoroborate. Chromatography of the crude product on silica plates developed with hexane–diethyl ether (9:1) gave the *ethylthiocyclopropanecarboxylate* **19b** (53%) as an oil (Found: M, 228.1175. $C_{12}H_{20}O_2S$ requires *M*, 228.1183); $\nu_{max}(CCl_4)/cm^{-1}$ 1713; $\delta_H$(200 MHz; $CDCl_3$) 1.18 (s, 2-Me), 1.18 (t, *J* 7.4, $SCH_2Me$), 1.26 (t, *J* 7.1, $OCH_2Me$), 1.31 and 1.68 (ABq, *J* 5.1, 3-$H_2$), 1.79 (dd, *J* 1.4 and 0.8, vinyl-Me), 2.53 (q, *J* 7.5, with fine splitting, $SCH_2$), 4.17 and 4.21 (qABq, *J* 7.1 and 10.8, $OCH_2$), 4.81 (quintet, *J* 0.8, C=$CH_2$) and 4.90 (quintet, *J* 1.5, C=$CH_2$); $\delta_C$(50.3 MHz; $CDCl_3$) 14.3, 14.4, 19.9, and 21.0 (4 × Me), 27.1 and 27.2 (2 × $CH_2$), 37.2 and 37.8 (C-1 and -2), 61.3 ($OCH_2$), 113.4 (C=$CH_2$), 145.7 (*C*=$CH_2$) and 171.8 (C=O).

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