*Tetrahedron* Vol. 46, No. 18, pp. 6525-6544, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00


# RHODIUM CARBENOID MEDIATED CYCLISATIONS. PART 6.[1] SYNTHESIS OF CYCLIC SULPHOXONIUM YLIDES

**Christopher J. Moody*[†] and Roger J. Taylor**

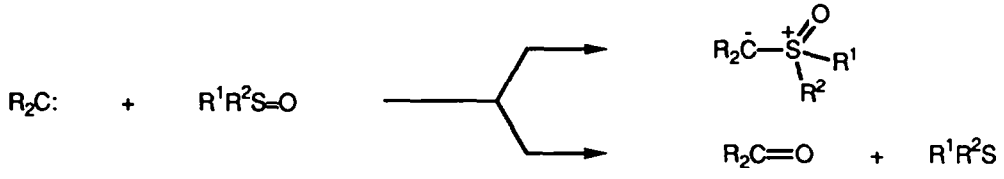
*Department of Chemistry, Imperial College of Science, Technology & Medicine, London SW7 2AY, UK.*

(*Received in UK* 21 *May* 1990)

*This paper is dedicated to Professor Wolfgang Kirmse on the occasion of his sixtieth birthday, in recognition of his outstanding contributions to carbene chemistry.*

**Summary**
Treatment of diazo sulphoxides with rhodium(II) acetate gives stable five- and six-membered cyclic sulphoxonium ylides.

The reaction of electron deficient nitrenes with sulphoxides is a general route to nitrogen-sulphoxonium ylides (sulphoximides).[2] Carbenes also react with sulphoxides to give sulphoxonium ylides,[3] although the reaction is complicated by competing attack of the carbene on oxygen resulting in deoxygenation of the sulphoxide (Scheme 1). Thus sulphoxonium ylides are formed in the copper(II)




**Scheme 1**

sulphate catalysed decomposition of ethyl diazoacetate in the presence of dimethyl- or diphenyl sulphoxide, and in the photochemical reactions of diethyl diazomalonate and sulphoxides.[3b] Similarly various ethyl diazoarylacetates have been thermolysed

[†]Present address: Department of Chemistry, Loughborough University of Technology, Loughborough, Leics, U.K.

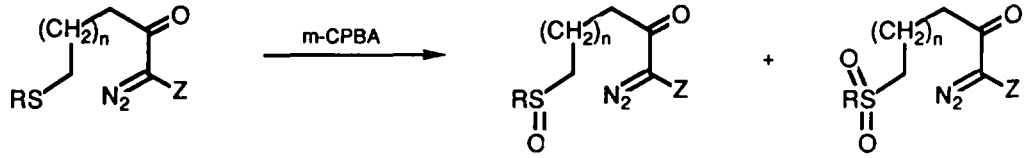
in the presence of dimethylsulphoxide and catalytic amounts of copper(I) cyanide to give good yields of sulphoxonium ylides.[3c] On the other hand, reaction of dichlorocarbene, generated under phase transfer conditions from chloroform, with sulphoxides leads to exclusive deoxygenation and the formation of sulphides.[4]

In the previous paper we have described the intramolecular interception of rhodium carbenoids by sulphides to give cyclic sulphonium ylides,[1] and we now report the full details of the first examples of intramolecular carbene-sulphoxide reaction to give cyclic sulphoxonium ylides.[5,6]

## RESULTS AND DISCUSSION

### *Preparation of Diazo Sulphoxides*

By analogy with our successful preparation of cyclic sulphonium ylides by the rhodium carbenoid mediated cyclisation of diazo sulphides,[1] the precursors to cyclic sulphoxonium ylides were diazo sulphoxides. 1,5 and 1,6-Diazo sulphoxides were prepared by oxidation of the corresponding diazo sulphides with 3-chloroperbenzoic acid (m-CPBA) in dichloromethane. Thus oxidation of the diazo sulphides (**1**), prepared as described in the previous paper,[1] gave the diazo sulphoxides (**2**) in good yield (53-84%) after work up with bisulphite and chromatography (Table 1). Over-oxidation to the sulphones (**3**) occurred as a minor side reaction. There was no evidence for the decomposition of the diazo group, indicating the robust nature of this functionality when flanked by 2 carbonyl groups.

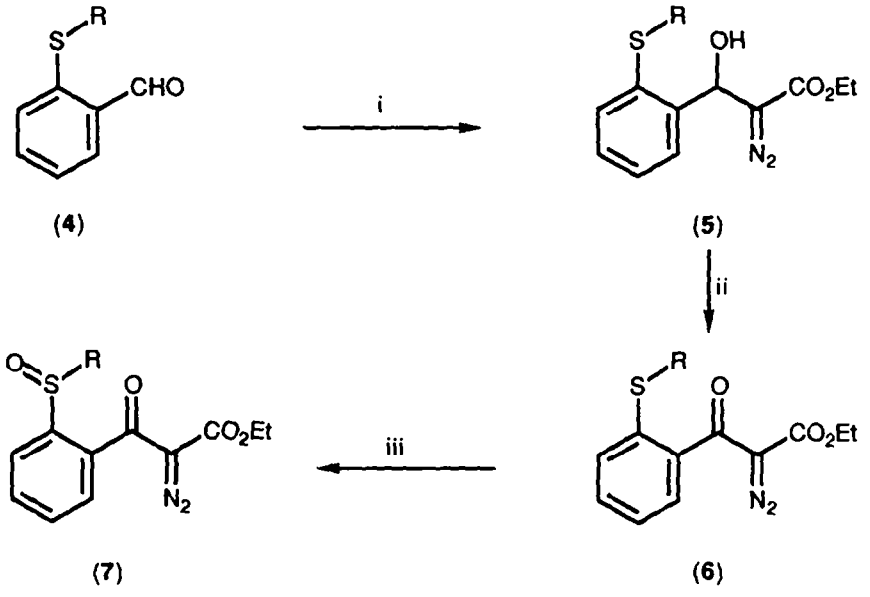



(1) (2) (3)

**Table 1.** Oxidation of diazosulphides

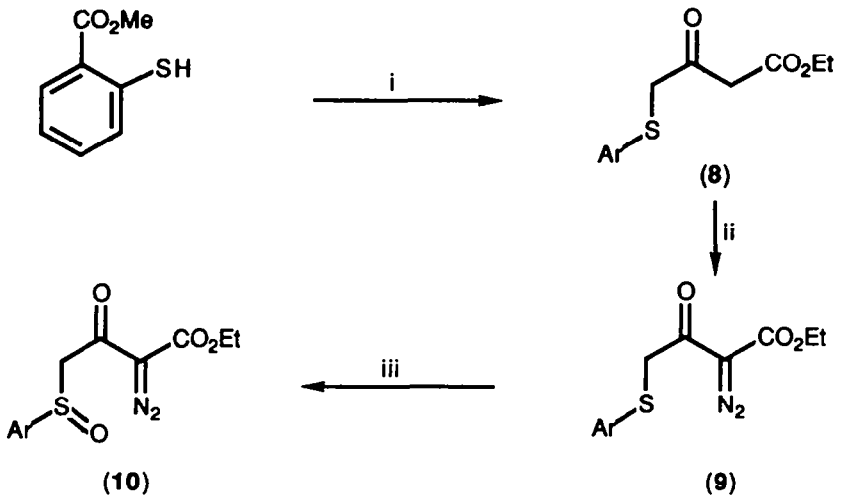
| *(1)-(3)* | *n* | *Z* | *R* | *Yield (2) (%)* | *Yield (3) (%)* |
|---|---|---|---|---|---|
| **a** | 1 | $CO_2Et$ | Et | 53 | 7 |
| **b** | 1 | $CO_2Et$ | $PhCH_2$ | 55 | - |
| **c** | 1 | $CO_2Et$ | $CH_2{=}CHCH_2$ | 54 | 20 |
| **d** | 1 | $CO_2Et$ | $PhCH{=}CHCH_2$ | 61 | 8 |
| **e** | 2 | $CO_2Et$ | $PhCH{=}CHCH_2$ | 60 | - |
| **f** | 2 | H | $PhCH_2$ | 84 | - |

An alternative strategy was developed for the synthesis of 1,4-diazosulphoxides, based on the reaction of ethyl lithiodiazoacetate with aromatic aldehydes as shown in Scheme 2. The reaction of benzaldehyde itself with ethyl lithiodiazoacetate has been reported to be high yielding,[7] and we found that the *ortho*-substituted benzaldehydes (**4**) reacted equally easily despite the bulk of the RS group. The alcohols (**5**) were oxidised to the corresponding α-diazo-β-keto esters (**6**) using barium manganate, which were further oxidised to the desired diazo sulphoxides (**7**) using m-CPBA. No over-oxidation to the corresponding sulphones was observed.




**Scheme 2** [**a**, R = Ph; **b** R = $PhCH_2$] *Reagents:* i, ethyl lithiodiazoacetate, THF, –75°C; ii, $BaMnO_4$, $CH_2Cl_2$; iii, m-CPBA, $CH_2Cl_2$.

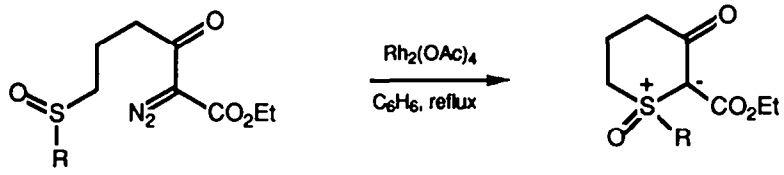
Finally the 1,3-diazo sulphoxide (**10**) was prepared from the ethyl ester of thiosalicylic acid and ethyl 4-chloroacetoacetate using conventional chemistry as shown in Scheme 3.




**Scheme 3** [Ar=2-$MeO_2C$-$C_6H_4$] Reagents: i, $ClCH_2COCH_2CO_2Et$, $Et_3N$, DMF; ii, $TsN_3$, $Et_3N$, MeCN; iii, m-CPBA, $CH_2Cl_2$.

*Rhodium(II) Catalysed Decomposition of Diazo Sulphoxides; Preparation of Cyclic Sulphoxonium Ylides.*

On heating in boiling benzene in the presence of a catalytic amount of rhodium(II) acetate the diazo sulphoxides (**2a-2d**) decomposed rapidly (< 2 min), and gave the cyclic ylides (**11a-11d**) in good yield (Table 2).




(2) (11)

**Table 2.** Preparation of 6-membered cyclic sulphoxonium ylides

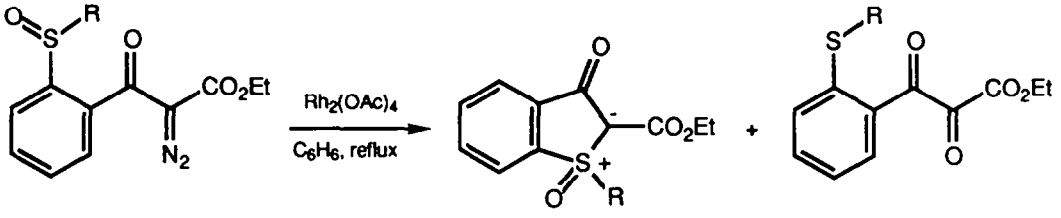
| *(2), (11)* | *R* | *Yield (11) (%)* | *m.p. (°C)* |
|---|---|---|---|
| **a** | Et | 78 | 174-177 |
| **b** | $PhCH_2$ | 76 | 175-177 |
| **c** | $CH_2$=$CHCH_2$ | 84 | 128-130 |
| **d** | PhCH=$CHCH_2$ | 54 | 143-144 |

The ylides (**11**) are all high melting, polar, crystalline solids, which exhibit spectroscopic properties consistent with their structure. In the case of ylide (**11c**), the structure was confirmed by *X*-ray crystallography which showed that the molecule adopts a half chair conformation with a pyramidal sulphur atom and the sulphoxide oxygen equatorial. In the crystal there is lengthening of both carbonyl C=O bonds, and a shortening of the ring C2-C3 bond indicating substantial stabilisation of the ylide by delocalisation of the negative charge.[8] This is also borne out by the IR spectra of the ylides which show two carbonyl absorptions at 1690 and 1630 $cm^{-1}$.

In contrast to the efficient formation of 6-membered ring sulphoxonium ylides from the 1,5-diazosulphoxides (**2a-2d**), rhodium(II) acetate catalysed decomposition of the 1,6-diazo sulphoxides (**2e**, **2f**) gave a complex mixture of products, with no evidence for the formation of the 7-membered ring sulphoxonium ylide.

Decomposition of the diazo sulphoxides (**7**), however, resulted in capture of the rhodium carbenoid by the sulphoxide sulphur, and formation of the 5-membered sulphoxonium ylides (**12a**) and (**12b**) in 70 and 58% yield respectively. The structures of the ylides (**12**) were supported by their spectroscopic properties, and in the case of (**12a**) confirmed by *X*-ray crystallography.[8]

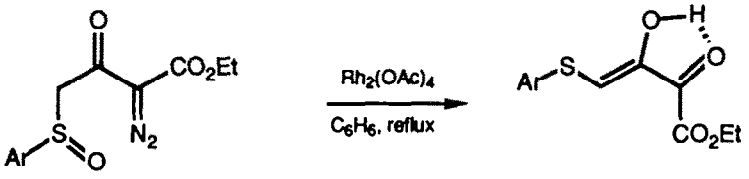
The ylides (**12**) were accompanied by small amounts of the tricarbonyl compounds (**13**), which are readily hydrated yellow oils. $^{1}H$ and $^{13}C$ n.m.r. spectroscopy showed the presence of both the keto and hydrated forms, although dehydration of the hydrate could be achieved *in vacuo* over phosphorus pentoxide, resulting in considerable simplification of the NMR spectra.




(**7**) (**12**) (**13**)

Hence both 6- and 5-membered cyclic sulphoxonium ylides can be prepared by intramolecular reactions of rhodium carbenoids with sulphoxides proceeding *via* 6- and 5-membered ring transition states respectively. In the latter case attack on oxygen *via* a 6-membered ring transition state is a competing, but minor, pathway.

However, when the diazosulphoxide (**10**) was decomposed under the usual conditions, attack on oxygen was the major pathway, and compound (**14**) was the only observed product (51%). Presumably the transition state required for the formation of a 4-membered cyclic sulphoxonium ylide is too strained, and therefore the oxygen transfer process, which occurs by a 5-membered transition state, supervenes.

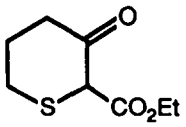



(**10**) (**14**)

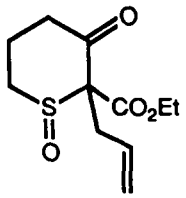
The product (**14**) is a yellow crystalline solid of molecular formula consistent with it being the oxygen transfer product. However, the spectroscopic data were not consistent with a tricarbonyl compound, showing *inter alia* a sharp O-H stretch at 3387 and two C=O stretches at 1715 and 1646 $cm^{-1}$ in its IR spectrum. The enolic structure (**14**) was supported by the $^1H$ NMR spectrum, its conversion into a t-butyldimethylsilyl enol ether, and confirmed by *X*-ray crystallography.[8]

*Reactions of Cyclic Sulphoxonium Ylides*

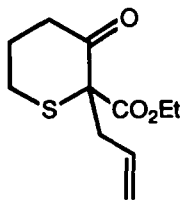
In contrast to cyclic sulphonium ylides,[1] the cyclic sulphoxonium ylides show less tendency to rearrange on heating. Thus the 5-membered ylides (**12**) were both stable to prolonged heating in refluxing mesitylene. The *S*-ethyl ylide (**11a**) was also stable to these conditions, showing no tendency to lose ethylene, although the *S*-benzyl compound (**11b**) slowly decomposed to a complex mixture of products. Likewise the *S*-allyl and *S*-cinnamyl ylides (**11c**) and (**11d**) decomposed on heating to give mixtures. The only identifiable component in the mixture obtained by heating ylide (**11c**) in refluxing xylene was the thiane (**15**),[1] derived from the ylide by loss of the allyl group and deoxygenation, presumably by [2,3]-sigmatropic rearrangement of the allyl group to the sulphoxide oxygen followed by β-elimination of acrolein. No other products could be identified, and the absence of sulphoxide (**16**), the product of [2,3]-sigmatropic rearrangement to carbon, was proved by its independent synthesis by oxidation of the thiane (**17**).[1]



(15)

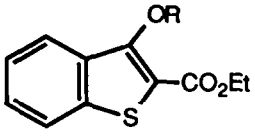


(16)

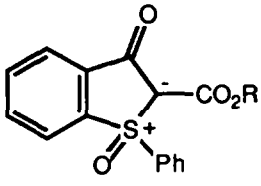


(17)

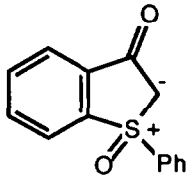
Photochemical decomposition of the cyclic sulphoxonium ylides was also investigated in the expectation that irradiation would lead to cleavage of the ylide bond to regenerate the sulphoxide and a photochemically excited carbene, which would presumably undergo Wolff rearrangement (*cf.* ref. 6b). In the event, irradiation of the ylide (**12b**) in ethanol gave a poor yield (31%) of a product assigned as the benzothiophene (**18**).[9] The structure was confirmed by acetylation to give (**19**) the melting point of which agreed with the literature value.[10] By analogy with the formation of (**15**) from (**11c**), the decomposition of (**12b**) involves the 1,2-migration of the benzyl group to the sulphoxide oxygen, followed by β–elimination of benzaldehyde.



(**18**) R = H
(**19**) R = Ac



(**12a**) R = Et
(**20**) R = H



(**21**)

The stability of the cyclic sulphoxonium ylide system to hydrolytic conditions was demonstrated by the hydrolysis of the ester in (**12a**) to the corresponding acid (**20**). The β-keto acid (**12**) was relatively stable, and only decarboxylated at its melting point (174-178°C). This decarboxylation could also be effected by heating a suspension of the acid (**20**) in xylene to reflux in the presence of acetic acid; no decarboxylation occurred in the absence of acetic acid. The product, formed in 88% yield, was the cyclic sulphoxonium ylide (**21**).

## EXPERIMENTAL

For general points, see refs 11 and 12. Diazo sulphide starting materials were prepared as described in ref. 1.

### *Preparation of Diazo Sulphoxides*

*General Procedure.*
A solution of the sulphide substrate (0.2-1 mmol) in dichloromethane (~10 ml) was cooled to -10°C, and m-chloroperbenzoic acid (m-CPBA) (85% tech; 1.1-1.3 eq.) was added batchwise over 10-30 min. After a further 10 min, the suspension was quenched with 10% aqueous sodium metabisulphite at -10°C. The dichloromethane phase was separated, washed with saturated sodium hydrogen carbonate, water, brine, and dried over magnesium sulphate. The crude product was purified by chromatography on silica gel to give the sulphoxide as the major product, together with some sulphone.

Ethyl 2-Diazo-6-ethylsulphinyl-3-oxohexanoate (**2a**).
m-CPBA (110 mg, 0.64 mmol) was added over 0.75 h to a solution of ethyl 2-diazo-6-ethylthio-3-oxohexanoate (**1a**) (131 mg, 0.536 mmol) in dichloromethane (12 ml) at -10°C. Work-up and purification gave the title compound (**2a**) (74 mg, 53%) as a low melting solid, m.p. 35-38°C; (Found: M$^+$, 260.0823. $C_{10}H_{16}N_2O_4S$ requires M, 260.0831); $\nu_{max.}$ (film) 2136, 1718, 1654, 1305, and 1020 cm$^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.31 (3 H, t, J 7.0 Hz), 1.32 (3 H, t, J 7.4 Hz), 2.11 (2 H, quin, J 7.1 Hz, $SCH_2CH_2$), 2.62-2.79 (4 H, m, $CH_2SCH_2$), 3.03 (2 H, dt, J 6.7, 1.9 Hz, $CH_2CO$), and 4.28 (2 H, q, J 6.9 Hz, $OCH_2$); m/z (140°C) 260 (M$^+$, 1%), 243 (1), 231 (8), 183 (26), 131 (10), 127 (39), 109 (57), 99 (33), 69 (41), and 29 (100); and a less polar component ethyl 2-diazo-6-ethylsulphonyl-3-oxohexanoate (**3a**) (10 mg, 7%) as an oil; (Found: M$^+$, 276.0771. $C_{10}H_{16}N_2O_5S$ requires M, 276.0780); $\nu_{max.}$ (film) 2139, 1717, 1653, 1379, 1305, and 1131 cm$^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.32 (3 H, t, J 7.1 Hz), 1.40 (3 H, t, J 7.4 Hz, $SCH_2CH_3$), 2.07-2.24 (2 H, m, $SCH_2CH_2$), 2.94-3.10 (6 H, m), and 4.29 (2 H, q, J 7.4 Hz, $CO_2CH_2$); m/z (80°C) 276 (M$^+$, 7%), 183 (3), 163 (49), 156 (21), 147 (64), 135 (21), 109 (19), and 69 (100).

Ethyl 6-Benzylsulphinyl-2-diazo-3-oxohexanoate (**2b**).
m-CPBA (57 mg, 0.33 mmol) was added over 10 min to a solution of ethyl 6-benzylthio-2-diazo-3-oxohexanoate (**1b**) (92 mg, 0.30 mmol) in dichloromethane

(10 ml) at -10°C. Work-up and purification gave the title compound (**2b**) (53 mg, 55%) as a low melting solid, m.p. 52-54°C; (Found: C, 56.0; H, 5.7; N, 8.7. $C_{15}H_{18}N_2O_4S$ requires C, 55.9; H, 5.6; N, 8.7%); $\nu_{max.}$ (melt) 2136, 1714, 1654, 1304, 1224, 1045, and 701 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.36 (3 H, t, J 7.1 Hz), 2.08-2.22 (2 H, m, $SCH_2CH_2$), 2.59-2.78 (2 H, m, $CH_2CO$), 3.03 (2 H, dt, J 6.9, 1.4 Hz, $SCH_2$), 4.02 (2 H, s, $PhCH_2$), 4.32 (2 H, q, J 7.1 Hz, $OCH_2$), 7.27-7.48 (5 H, m, ArH); m/z (C.I.; $NH_3$) 323 ($MH^+$, 67%), 295 (36), 91 (100).

Ethyl 6-Allylsulphinyl-2-Diazo-3-oxohexanoate (**2c**).
A solution of ethyl 6-allylthio-2-diazo-3-oxohexanoate (**1c**) (196 mg, 0.765 mmol) in dichloromethane (7 ml) at 0°C was buffered with anhydrous disodium hydrogen phosphate (0.9 g), and then treated with m-CPBA (0.21 g, 1.15 mmol) over 0.25 h. Work-up and purification gave the title compound (**2c**) (112 mg, 54%) as a viscous polar oil; (Found: C, 48.5; H, 6.1; N, 10.2. $C_{11}H_{16}N_2O_4S$ requires C, 48.5; H, 5.9; N, 10.3%); $\nu_{max.}$ (film) 2136, 1717, 1654, 1377, 1305, and 1041 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.25 (3 H, t, J 7.1 Hz), 2.06 (2 H, quin, J 7.2 Hz, $CH_2CH_2S$), 2.62-2.75 (2 H, m, $CH_2S$), 2.97 (2 H, dt, J 6.9, 1.5 Hz, $CH_2CO$), 3.34 (1 H, ddt, J 12.5, 6.8, 0.6 Hz, $SCH_2CH$), 3.46 (1 H, ddt, J 12.5, 6.8, 0.6 Hz, $SCH_2CH$), 4.23 (2 H, q, J 7.1 Hz, $CO_2CH_2$), 5.26-5.43 (2 H, m, $CH_2$:CH), and 5.83 (1 H, ddt, J 16.5, 10.2, 7.4 Hz, $CHCH_2S$); m/z (120°C) 272 ($M^+$, 1%), 256 (1), 231 (100), 227 (3), 203 (2), 159 (10), 127 (21), 109 (19), and 41 (86); and a less polar product, ethyl 6-allylsulphonyl-2-diazo-3-oxohexanoate (**3c**) (43 mg, 20%) as an oil; (Found: $M^+$, 260.0718. $C_{11}H_{16}N_2O_5S$ $-N_2$ requires M, 260.0660); $\nu_{max.}$ (film) 2138, 1714, 1652, 1380, 1306, and 1132 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.27 (3 H, t, J 7.1 Hz), 2.12 (2 H, quin, J 7.3 Hz, $SCH_2CH_2$), 2.92-3.07 (4 H, m, $SCH_2CH_2CH_2CO$), 3.68 (2 H, d, J 7.0 Hz, $CHCH_2S$), 4.25 (2 H, q, J 7.1 Hz, $OCH_2$), 5.36-5.50 (2 H, m), and 5.89 (1 H, ddt, J 16.9, 10.6, 7.2 Hz); m/z (160°C) 288 ($M^+$, 1%), 260 (1), 247 (1), 243 (1), 224 (1), 196 (5), 159 (14), 109 (16), 41 (100).

Ethyl 2-Diazo-3-oxo-6-(3-phenylprop-2-enyl)sulphinylhexanoate (**2d**).
m-CPBA (210 mg, 1.2 mmol) was added over 1 h to a solution of ethyl 2-diazo-3-oxo-6-(3-phenylprop-2-enyl)thiohexanoate (**1d**) (335 mg, 1.01 mmol) in dichloromethane (30 ml). Work up and purification gave the title compound (**2d**) (212 mg, 61%) as a solid, m. p. 81-83°C; (Found: C, 58.5; H, 5.8; N, 7.8. $C_{17}H_{20}N_2O_4S$ requires C, 58.6; H, 5.8; N, 8.0%); $\nu_{max.}$ (melt) 2136, 1714, 1651, 1376, 1304, 1224, and 1039 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.29 (3 H, t, J 7.0 Hz, $CH_2CH_3$), 2.12 (2 H, m, $SCH_2CH_2$), 2.70-2.82 (2 H, m, $CH_2CH_2S$), 3.01 (2 H, dt, J 7.0, 1.0 Hz, $CH_2CO$), 3.56 (1

H, ddd, J 12.5, 7.5 ,0.8 Hz, $CHCH_2S$), 3.67 (1 H, ddd, J 12.5, 7.5, 0.8 Hz, $CHCH_2S$), 4.26 (2 H, q, J 7.0 Hz, $CO_2CH_2$), 6.24 (1 H, dt, J 15.5, 7.2 Hz, CHCHPh), 6.65 (1 H, d, J 15.5 Hz, CHPh), and 7.20-7.43 (5 H, m, ArH); m/z (FAB; glycerol) 349 ($MH^+$, 4%), 155 (2), 117 (100), and 91 (7); and a less polar product ethyl 2-diazo-3-oxo-6-(3-phenylprop-2-enyl)sulphonylhexanoate (**3d**) (28 mg, 8%) as an oil; (Found: C, 56.1; H, 5.7; N, 7.6. $C_{17}H_{20}N_2O_5S$ requires C, 56.0; H, 5.5; N, 7.7%); $\nu_{max.}$ (film) 2138, 1714, 1652, 1379, 1304, 1225, 1122, 971, and 745 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.30 (3 H, t, J 7.0 Hz, $CH_2CH_3$), 2.10-2.24 (2 H, m, $CH_2CH_2S$), 2.95-3.09 (4 H, m, $SCH_2CH_2CH_2CO$), 3.85 (2 H, d, J 7.3 Hz, $CHCH_2S$), 4.26 (2 H, q, J 7.0 Hz, $CO_2CH_2$), 6.24 (1 H, dt, J 15.5, 7.2 Hz, PhCHCH), 6.72 (1 H, d, J 15.5 Hz, PhCH), 7.21-7.47 (5 H, m, ArH); m/z (FAB; glycerol) 365 ($MH^+$, 1%), 215 (1), 203 (2), 185 (3), 117 (100), and 91 (16).

Ethyl 2-Diazo-3-oxo-7-(3-phenylprop-2-enyl)sulphinylheptanoate (**2e**).
m-CPBA (108 mg, 0.62 mmol) was added over 20 min to a solution of ethyl 2-diazo-3-oxo-7-(3-phenylprop-2-enyl)thioheptanoate (**1e**) (180 mg, 0.52 mmol) in dichloromethane (10 ml) at -11°C. Work-up and purification gave the title compound (**2e**) (113 mg, 60%) as a low melting solid, m.p. 48-50°C; (Found: C, 59.7; H, 6.2; N, 7.7. $C_{18}H_{22}N_2O_4S$ requires C, 59.7; H, 6.1; N, 7.7%); $\nu_{max.}$ (melt) 2135, 1714, 1652, 1450, 1372, 1305, 1218, 1025, and 748 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.32 (3 H, t, J 7.0 Hz, $CH_2CH_3$), 1.70-1.94 (4 H, m), 2.75 (2 H, approx t, J 7.1 Hz, $CH_2CH_2S$), 2.90 (2 H, approx t, J 6.7 Hz, $CH_2CO$), 3.53-3.73 (2 H, m, $CHCH_2S$), 4.28 (2 H, q, J 7.0 Hz, $CO_2CH_2$), 6.25 (1 H, dt, J 15.6, 7.8 Hz, PhCHCH), 6.68 (1 H, d, J 15.8 Hz, PhCH), and 7.22-7.44 (5 H, m, ArH); m/z (FAB; glycerol) 363 ($M^+$, 4%), 337 (1), 165 (1), 147 (1), 129 (2), 117 (100), 91 (14).

6-Benzylsulphinyl-1-diazohexan-2-one (**2f**).
A solution of 6-benzylthio-1-diazohexan-2-one (**1f**) (57 mg, 0.23 mmol) in dichloromethane (10 ml) at -20°C was buffered with anhydrous disodium hydrogen phosphate (0.2 g) and then treated with m-CPBA (43 mg, 0.25 mmol) over 0.2 h. Work up and purification by chromatography on Florisil gave the title compound (**2f**) (51 mg, 84%) as a solid, m.p. 71-74°C; $\nu_{max.}$ (melt) 3080, 2119, 1623, 1387, 1022, 699 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.64-1.89 (4 H, m), 2.27-2.42 (2 H, m, $CH_2CO$), 2.57 (2 H, approx t, J 7.1 Hz, $CH_2S$), 3.93 (1 H, d, J 12.9 Hz, $CH_2Ph$), 4.05 (1 H, d, J 12.9 Hz, $CH_2Ph$), 5.23 (1 H, br, $CHN_2$), and 7.23-7.43 (5 H, m, ArH).

Ethyl 2-Diazo-3-hydroxy-3-(2-phenylthio)phenylpropanoate (**5a**).
A solution of LDA (6.68 mmol) in THF (10 ml), prepared by the addition of n-butyllithium in hexane (4.03 ml, 6.68 mmol) to diisopropylamine (0.94 ml, 6.68 mmol) in THF (10 ml) at 0°C, was added dropwise by catheter to a solution of ethyl diazoacetate (0.87 g, 7.59 mmol) and 2-(phenylthio)benzaldehyde (**4a**) (1.30 g, 6.07 mmol) in THF (30 ml) at -75°C over 0.25 h. After stirring for 1.5 h, acetic acid (0.5 ml) was added and the solution allowed to warm to 0°C, before the addition of water. Work-up and purification by chromatography on silica gel gave the title compound (**5a**) (1.93 g, 97%) as a yellow solid, m.p. 69-70°C (dec.); (Found: C, 62.4; H, 4.9; N, 8.4. $C_{17}H_{16}N_2O_3S$ requires C, 62.2; H, 4.9; N, 8.5%); $\nu_{max.}$ (melt) 3439, 2097, 1674, 1295, 1108, and 741 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.23 (3 H, t, J 7.1 Hz, $CH_2CH_3$), 3.44 (1 H, br, OH), 4.07-4.29 (2 H, m, $COCH_2$), 6.32 (1 H, d, J 3.1 Hz, CHOH), 7.10-7.47 (8 H, m), and 7.74 (1 H, d, J 6.7 Hz); m/z (100°C) 300 ($M^+$-$N_2$, 77%), 283 (100), 254 (24), 226 (48), 213 (69), 197 (75), 184 (46), 137 (41)

Ethyl 3-(2-Benzylthio)phenyl-2-diazo-3-hydroxypropanoate (**5b**).
A solution of LDA (4.62 mmol) in THF (10 ml), prepared by the addition of n-butyl lithium in hexane (2.93 ml, 4.62 mmol) to diisopropylamine (0.68 ml, 4.84 mmol) in THF (10 ml) at 0°C, was added dropwise by catheter to a solution of ethyl diazoacetate (0.553 g, 4.84 mmol) and 2-(benzylthio)benzaldehyde (**4b**) (1.01 g, 4.40 mmol) in THF (25 ml) at -75°C over 0.25 h. After stirring for 1.5 h, acetic acid (0.4 ml) was added and the solution allowed to warm to 0°C, before the addition of water and subsequent extraction of organic material into dichloromethane. The dichloromethane phase was washed with water, then brine and finally dried over magnesium sulphate. After evaporation, the residue was purified by chromatography on silica gel to give the title compound (**5b**) (1.38 g, 92%) as a yellow oil which solidified at 0°C; (Found: C, 63.2; H, 5.3; N, 8.0. $C_{18}H_{18}N_2O_3S$ requires C, 63.1; H, 5.3; N, 8.2%); $\nu_{max.}$ (film) 3441, 2097, 1675, 1373, 1294, 1107, and 749 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.28 (3 H, t, J 7.0 Hz, $CH_2CH_3$), 3.00 (1 H, br, OH), 4.05 (1 H, d, J 12.3 Hz, $CH_2Ph$), 4.12 (1 H, d, J 12.3 Hz, $CH_2Ph$), 4.26 (2 H, dq, J 7.0, 2.0 Hz, $CO_2CH_2$), 6.11 (1 H, d, J 3.2 Hz, CHOH), and 7.11-7.65 (9 H, m, ArH); m/z (150°C) 314 ($M^+$-$N_2$, 4%), 296 (7), 228 (14), 223 (34), 206 (21), 161 (22),137 (21), and 91 (100).

Ethyl 2-Diazo-3-oxo-3-(2-phenylthio)phenylpropanoate (**6a**).
Barium manganate (2.5 g, 9.8 mmol) was added to a solution of (**5a**) (1.55g, 4.71 mmol) in dichloromethane (50 ml) and the suspension stirred rapidly for 15 h at room temperature, and then heated at reflux for 3 h. The reaction mixture was

filtered through Celite, evaporated, and the residue subjected to chromatography to give the title compound (**6a**) (1.06 g, 91%) as a yellow oil; ( Found: M$^+$, 326.0717. $C_{17}H_{14}N_2O_3S$ requires M, 326.0725); $\nu_{max.}$ (film) 2143, 1724, 1635, 1317, and 750 cm$^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.18 (3 H, t, J 7.1 Hz, $CO_2CH_2CH_3$), 4.18 (2 H, q, J 7.1 Hz, $CO_2CH_2CH_3$), and 7.16-7.46 (9 H, m, ArH); m/z (100°C) 326 (M$^+$, 1%), 300 (1), 253 (5), 225 (100), 197 (50), and 176 (27).

Ethyl 3-(2-Benzylthio)phenyl-2-diazo-3-oxopropanoate (**6b**).
Barium manganate (1.8 g, 6.9 mmol) was added to a solution of (**5b**) (1.18g, 3.44 mmol) in dichloromethane (50 ml) and the suspension stirred rapidly for 12 h at room temperature. More barium manganate (0.88 g, 3.44 mmol) was added and the suspension heated at reflux for 6 h. The reaction mixture was filtered through Celite, evaporated, concentrated, and the residue subjected to chromatography to give the title compound (**6b**) (1.35 g, 88%) as a yellow oil; ( Found: C, 63. 4; H, 4.7; N, 8.4. $C_{18}H_{16}N_2O_3S$ requires C, 63.5; H, 4.7; N, 8.2%); $\nu_{max.}$ (film) 2142, 1724, 1694, 1634, 1370, 1304, 1118, and 752 cm$^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.16 (3 H, t, J 6.8 Hz, $CO_2CH_2CH_3$), 4.06 (2 H, s, $CH_2Ph$), 4.16 (2 H, q, J 6.8 Hz, $CO_2CH_2$), and 7.22-7.35 (9 H, m, ArH); m/z (FAB; glycerol) 341 (MH$^+$, 1%), 313 (1), 277 (2), 239 (4), 227 (4), 211 (3), 185 (26), and 91 (100).

Ethyl 2-Diazo-3-oxo-3-(2-phenylsulphinyl)phenylpropanoate (**7a**).
m-CPBA (0.82 g, 4.8 mmol) was added over 0.5 h to a solution of (**6a**) (1.30 g, 4.00 mmol) in dichloromethane (25 ml) at -15°C. Work-up and purification gave the title compound (**7a**) (1.16 mg, 85%) as a yellow solid, m.p. 94-95°C; (Found: C, 59.4; H, 4.0; N, 8.0. $C_{17}H_{14}N_2O_4S$ requires C, 59.6; H, 4.1; N, 8.2%); $\nu_{max.}$ (melt) 2147, 1724, 1625, 1304, 1041, and 751 cm$^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.16 (3 H, t, J 7.1 Hz, $CO_2CH_2CH_3$), 4.15 (2 H, q, J 7.1 Hz, $CO_2CH_2CH_3$), 7.12-7.78 (8 H, m, ArH), and 8.08 (1 H, d, J 7.6 Hz, ArH); m/z (FAB; glycerol) 343 (MH$^+$, 3%), 315 (19), 299 (6), 269 (25), 229 (23), 213 (23), 185 (43), and 93 (100).

Ethyl 3-(2-Benzylsulphinyl)phenyl-2-diazo-3-oxopropanoate (**7b**).
m-CPBA (0.58 g, 3.4 mmol) was added over 0.5 h to a solution of (**6b**) (0.960 g, 2.82 mmol) in dichloromethane (25 ml) at -13°C. Work-up and purification gave the title compound (**7b**) (868 mg, 86%) as a viscous oil; (Found: C, 61.0; H, 4.7; N, 7.9. $C_{18}H_{16}N_2O_4S$ requires C, 60.7; H, 4.5; N, 7.9%); $\nu_{max.}$ (film) 2148, 1724, 1619, 1321, 1271, and 752 cm$^{-1}$; $\delta_H$ (60 MHz; $CDCl_3$) 1.22 (3 H, t, J 6.4 Hz, $CO_2CH_2CH_3$), 4.02 (1 H, d, J 11.0 Hz, $CH_2Ph$), 4.19 (2 H, q, J 6.4 Hz, $CO_2CH_2CH_3$), 4.40 (1 H, d, J 11.0 Hz,

$CH_2Ph$), and 6.95-7.88 (9 H, m, ArH); m/z (FAB; glycerol) 357 ($MH^+$, 6%), 331 (12), 277 (4), 223 (7), 185 (48), and 93 (100).

Ethyl 4-[(2-Methoxycarbonylphenyl)thio]-3-oxobutanoate (**8**).
Triethylamine (0.18 ml, 1.30 mmol) was added dropwise to a stirred solution of methyl 2-mercaptobenzoate (182 mg, 1.08 mmol) and ethyl 4-chloroacetoacetate (0.155 ml, 1.14 ml) in DMF (3 ml). After 1 h, the reaction mixture was subjected to aqueous work-up and chromatography to give the title compound (**8**) (308 mg, 96%) as colourless crystals, m.p. 52-53°C; (Found: C, 56.4; H, 5.4. $C_{14}H_{16}O_5S$ requires C, 56.7; H, 5.4%); $\nu_{max.}$ (melt) 1744, 1713, 1280, 1255, 1029, and 745 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.24 (3 H, t, J 6.9 Hz, $CH_2CH_3$), 3.66 (2 H, s, $SCH_2$), 3.88 (2 H, s, $O_2CCH_2$), 3.92 (3 H, s, $CO_2CH_3$), 4.16 (2 H, q, J 6.9 Hz, $CO_2CH_2$), 7.21 (1 H, dt, J 7.5, 0.5 Hz), 7.29 (1 H, dd, J 7.7, 0.5 Hz), 7.41-7.51 (1 H, m), 8.00 (1 H, dd, J 8.0, 1.5 Hz); m/z (150°C) 296 ($M^+$, 10%), 224 (33), 181 (47), 150 (42), 45 (100).

Ethyl 2-Diazo-4-[(2-methoxycarbonylphenyl)thio]-3-oxobutanoate (**9**).
Triethylamine (0.154 ml, 1.10 mmol) was added dropwise to a solution of tosyl azide (216 mg, 1.10 mmol) and (**8**) (295 mg, 0.997 mmol) in acetonitrile (3 ml) at -10°C, to give an immediate precipitate. After 0.25 h, the reaction mixture was allowed to warm to 4°C and stirred for 12 h. The solvent was evaporated, dichloromethane added and the organic phase washed with saturated sodium hydrogen carbonate solution and brine. The dichloromethane was evaporated and the crude product purified by chromatography to give the title compound (**9**) (142 mg, 44%) as colourless crystals, m.p. 105-110°C (dec.); (Found: $M^+$, 322.0622. $C_{14}H_{14}N_2O_5S$ requires M, 322.0623); $\nu_{max.}$ (Nujol) 2138, 1712, 1651, 1328, 1283, 1252, and 744 $cm^{-1}$; $\delta_H$ (270 MHz; $CDCl_3$) 1.33 (3 H, t, J 7.1 Hz, $CH_2CH_3$), 3.91 (3 H, s, $CO_2CH_3$), 4.25 (2 H, s, $SCH_2$), 4.35 (2 H, q, J 7.1 Hz, $CO_2CH_2$), 7.20 (1 H, dt, J 7.0, 1 Hz), 7.45 (1 H, dt, J 7.0, 1 Hz), 7.55 (1 H, dd, J 7.0, 1 Hz), and 7.95 (1 H, dd, J 7.3 Hz); m/z (100°C) 322 ($M^+$, 29%), 294 (22), 265 (12), 235 (14), 219 (16), 181 (31), 168 (32), 136 (74), and 45 (100).

Ethyl 2-Diazo-4-[(2-methoxycarbonylphenyl)sulphinyl]-3-oxobutanoate (**10**).
m-CPBA (61 mg, 0.35 mmol) was added to a solution of (**9**) (95 mg, 0.295 mmol) in dichloromethane (10 ml) at -10°C over 0.5 h. Work-up and purification gave the title compound (**10**) (93 mg, 93%) as a viscous oil; (Found: C, 49.5; H, 4.1; N, 8.4. $C_{14}H_{14}N_2O_6S$ requires C, 49.7; H, 4.2; N, 8.3%); $\nu_{max.}$ (film) 2139, 1713, 1651, 1396,

1328, 1289, and 1027 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.27 (3 H, t, J 7 0 Hz, $CH_2CH_3$), 3.92 (3 H, s, $CO_2CH_3$), 4.23 (2 H, q, J 7.0 Hz, $CO_2CH_2$), 4.35 (1 H, d, J 14.3 Hz, $SCH_2$), 4.62 (1 H, d, J 14.6 Hz, $SCH_2$), 7.58 (1 H, dt, J 7.5, 1.3 Hz), 7.81 (1 H, dt, J 7.8, 1.3 Hz), 8.07 (1 H, dd, J 7.5, 1.1 Hz), and 8.27 (1 H, dd, J 8.0, 1.1 Hz); m/z (100°C) 338 ($M^+$, 1%), 310 (3), 293 (3), 262 (2), 209 (15), 183 (100), 167 (36), 152 (81), 139 (56).

### *Rhodium (II) Catalysed Decomposition of Diazo Sulphoxides*

Ethyl 1-Ethyl-3-oxothiane-1-oxide-2-carboxylate, inner salt (**11a**).
A solution of (**2a**) (60 mg, 0.23 mmol) in benzene (5 ml) was added to a suspension of dirhodium tetraacetate (1.1 mg) in benzene (7.5 ml) over 7 min. After 1 min at reflux the suspension was cooled, filtered, evaporated, and the residue recrystallised to give the title compound (**11a**) (42 mg, 78 %) as colourless crystals, m.p. 174-177°C (benzene/ether); (Found: $M^+$, 232.0773. $C_{10}H_{16}O_4S$ requires M, 232.0769); $\nu_{max.}$ (Nujol) 1723, 1655, 1373, 1207, 1054, and 756 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.30 (3 H, t, J 7.0 Hz, $OCH_2CH_3$), 1.40 (3 H, J 7.3 Hz, $SCH_2CH_3$), 2.12-2.60 (4 H, m, $CH_2CH_2CO$), 3.27-3.54 (2 H, m, $CH_2CH_2S$), 3.97 (2 H, approx. q, J 7.5 Hz, $CH_3CH_2S$), and 4.13-4.34 (2 H, m, $CO_2CH_2$); m/z (180°C) 232 ($M^+$, 100%), 187 (41), 162 (40), 159 (23), 134 (31), 116 (23), 111(15).

Ethyl 1-Benzyl-3-oxothiane-1-oxide-2-carboxylate, inner salt (**11b**).
A solution of (**2b**) (62 mg, 0.194 mmol) in benzene ( 5 ml) was added to a suspension of dirhodium tetraacetate (1 mg) in benzene (10 ml) at reflux over 0.2 h. After 5 min at reflux, the suspension was cooled, filtered, evaporated, and the residue recrystallised to give the title compound (**11b**) (43mg, 76%) as colourless crystals, m.p. 175-177°C (benzene/dichloromethane) (Found: C, 61.0; H, 6.0. $C_{15}H_{18}O_4S$ requires C, 61.2; H, 6.2%); $\nu_{max.}$ (Nujol) 1633, 1611, 1319, 1250, 1208, and 1126 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.39 (3 H, t, J 6.8 Hz, $CH_2CH_3$), 1.86-2.00 (1 H, m), 2.08-2.55 (3 H, m), 3.04 (1 H, dd, J 13.1, 5.6 Hz, $CH_2CH_2S$), 3.30 (1 H, dt, J 12.5, 2.8 Hz, $CH_2CH_2S$), 4.26-4.44 (2 H, m, $CO_2CH_2$), 5.23 (1 H, d, J 13.5 Hz, $PhCH_2$), 5.32 (1 H, d, J 13.5 Hz, $PhCH_2S$), and 7.45 (5 H, m, ArH); m/z (190°C) 294 ($M^+$, 2%), 248 (3), 204 (3), 187 (12), 142 (13), 103 (9), 91 (100).

Ethyl 1-Allyl-3-oxothiane-1-oxide-2-carboxylate, inner salt (**11c**).
A solution of (**2c**) (114 mg, 0.419 mmol) in benzene (6 ml) was added dropwise to a

suspension of dirhodium tetraacetate (5 mg) in benzene (10 ml) at reflux over 6 min. After 0.2 h at reflux the suspension was cooled, filtered, evaporated, and the residue recrystallised to give the title compound (**11c**) (81 mg, 84%) as colourless crystals, m.p. 128-130°C (benzene/ethyl acetate); (Found: C, 53.8; H, 6.6; S, 13.1. $C_{11}H_{16}O_4S$ requires C, 54.1; H, 6.6; S, 13.1%); $\nu_{max.}$ (Nujol) 1697, 1574, 1370, 1336, and 1190 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.33 (3 H, t, J 6.9 Hz, $CH_2CH_3$), 2.10-2.63 (4 H, m, $CH_2CH_2CO$), 3.21-3.47 (2 H, m, $SCH_2$), 4.21-4.37 (2 H, m, $CO_2CH_2$), 4.53 (1 H, dd, J 10.1, 7.5 Hz, $CHCH_2$), 4.78 (1 H, dd, J 10.1, 6.6 Hz, $CHCH_2$), 5.50-5.62 (2 H, m, [illegible]

Ethyl 3-oxo-1-(3-Phenylprop-2-enyl)thiane-1-oxide-2-carboxylate, inner salt (**11d**).

A solution of (**2d**) (200 mg, 0.574 mmol) in benzene (7 ml) was added to a suspension of dirhodium tetraacetate (4 mg) in benzene (20 ml) over 1 min. After 1 min at reflux, the suspension was cooled, filtered, evaporated, and the residue recrystallised to give the title compound (**11d**) (100 mg, 54%) as a colourless solid, m.p. 143-144°C (benzene); (Found: C, 63.5; H, 61.9; S, 9.7. $C_{17}H_{20}O_4S$ requires C, 63.7; H, 6.3; S, 10.0%); $\nu_{max.}$ (Nujol) 1692, 1576, 1462, 1374, 1202, and 756 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.37 (3 H, t, J 7.1 Hz, $CH_2CH_3$), 2.10-2.63 (4 H, m, $CH_2CH_2CO$), 3.26-3.39 (1 H, m, $CH_2CH_2S$), 3.40-3.56 (1 H, m, $CH_2CH_2S$), 4.21-4.44 (2 H, m, $CO_2CH_2$), 5.85 (1 H, dd, J 14.5, 8.0 Hz, $CHCH_2S$), 5.94 (1 H, dd, J 14.5, 8.0 Hz , $CHCH_2S$), 6.12 (1 H, dt, J 15.5, 7.0 Hz, PhCHCH), 6.83 (1 H, d, J 15.5 Hz, PhCH), and 7.21-7.53 (5 H, m, ArH); m/z (130°C) 320 ($M^+$, 4%), 304 (1), 286 (1), 274 (25), 188 (30), 142 (46), 129 (45), 117 (100), 105 (87), and 77 (64).

Ethyl 2,3-Dihydro-3-oxo-1-phenylbenzo[b]thiophene-1-oxide-2-carboxylate, inner salt (**12a**)

Dirhodium tetraacetate (4 mg) was added to a solution of (**7a**) (1.13 g, 3.29 mmol) in benzene (30 ml) which had been rapidly heated to reflux. After 2 min at reflux, the yellow coloured solution was cooled, evaporated, dichloromethane (5 ml) added and the catalyst removed by filtration through Celite. The filtrate was evaporated, and the residue recrystallised to give the title compound (**12a**) as colourless crystals, m.p. 175-176°C (benzene); (Found: C, 65.0; H, 4.4. $C_{17}H_{14}O_4S$ requires C, 65.0; H, 4.5%); $\nu_{max.}$ (Nujol) 1719, 1656, 1606, 1370, 1196, 1040 and 771 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.17 (3 H, t, J 6.9 Hz, $CO_2CH_2CH_3$), 4.00-4.29 (2 H, m, $CO_2CH_2$), 7.54-7.74 (5 H, m, PhH), 7.80 (1 H, dt, J 7.4, 0.8 Hz), 7.90 (2 H, m), and 8.02 (1 H, d, J 7.5 Hz); $\delta_C$ (62.9 MHz; $CDCl_3$) 13.8, 59.2, 85.0, 122.9, 123.0, 124.0, 127.6, 129.8,

133.2, 134.1, 134.2, 135.4, 136.3, 161.0, and 175.0; m/z (190°C) 314 ($M^+$, 54%), 269 (97), 213 (100), 197 (18), 177 (30), 136 (62), 118 (78), and 77 (60). The mother liquor from the recrystallisation was subjected to chromatography and gave a second component ethyl 2,3-dioxo-3-(2-phenylthio)phenylpropanoate (**13a**) (194 mg, 19%) as a yellow and readily hydrated oil; (Found: C, 64.8; H, 4.8; S, 10.5. $C_{18}H_{16}O_4S$ requires C, 65.0; H, 4.5; S, 10.2%); $\nu_{max.}$ (film) 3423, 1747, 1720, 1675, 1585, 1463, 1300, 1233, 1100, 1069, 1047, 1016, and 743 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.11 (3 H, t, J 7.0 Hz, $CO_2CH_2CH_3$ hydrate), 1.26 (3 H, t, J 7.0 Hz, $CO_2CH_2CH_3$ keto), 4.23 (2 H, q, J 6.9Hz, $CO_2CH_2$ hydrate), 4.29 (2 H, q, J 6.9 Hz, $CO_2CH_2$ keto), 5.36 (2 H, br, OH hydrate), 6.86 (1 H, dd, J 7.8, 1.0 Hz, ArH hydrate), 7.05-7.60 (~7 H, m, ArH), 7.98 (1 H, dd, J 7.8, 1.9 Hz, ArH keto), and 8.00 (1 H, dd, J 7.8, 1.6 Hz, ArH hydrate); $\delta_C$ (62.9 MHz; $CDCl_3$) 13.0, 13.2, 62.4, 62.6, 92.3, 124.0, 127.9, 128.1, 128.3, 128.7, 129.1, 129.3, 129.6, 130.0,131.3, 131.6, 132.5, 133.0, 133.8, 134.4, 134.6, 135.0, 135.5, 137.2, 145.5, 159.3, 169.8, 180.7, 191.6, and 192.2; m/z (150°C) 314 ($M^+$, 5%), 227 (1), 213 (100), 184 (19), 152 (3), and 139 (2).

Ethyl 1-Benzyl-2,3-dihydro-3-oxobenzo[b]thiophene-1-oxide-2-carboxylate, inner salt (**12b**)

Dirhodium tetraacetate (4 mg) was added to a solution of (**7b**) (554 mg, 1.56 mmol) in benzene (30 ml) which had been rapidly heated to reflux. After 2 min at reflux, the yellow coloured solution was cooled, evaporated, dichloromethane (5 ml) added and the catalyst removed by filtration through Celite. The filtrate was evaporated, and the residue recrystallised to give the title compound (**12b**) as colourless crystals, m.p. 168-172°C (benzene); (Found: C, 65.8; H, 4.8. $C_{18}H_{16}O_4S$ requires C, 65.8; H, 4.9%); $\nu_{max.}$ (Nujol) 1714, 1630, 1374, 1345, 1211, 1075, and 762 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.45 (3 H, t, J 7.1 Hz, $CO_2CH_2CH_3$), 4.38 (2 H, m, $CO_2CH_2$), 5.16 (1 H, d, J 13.5 Hz, $CH_2Ph$), 5.36 (1 H, d, J 13.5 Hz, $CH_2Ph$), 7.05-7.12 (2 H, m, $CH_2Ph$), 7.19-7.36 (3 H, m, $CH_2Ph$), 7.61 (1 H, approx d, J 7.1 Hz), 7.69 (1 H, dt, J 7.3, 1.5 Hz), 7.77 (1 H, dt, J 7.3, 1.5 Hz), and 7.83 (1 H, approx d, J 7.7 Hz); m/z (160°C) 328 ($M^+$, 1%), 312 (1), 282 (1), 255 (1), 227 (53), 176 (5), 136 (5), and 91(100). The mother liquor from the recrystallization was subjected to chromatography and gave a second component ethyl 3-(2-benzylthio)phenyl-2,3-dioxopropanoate (**13b**) (30 mg, 6%) as a yellow and readily hydrated oil; (Found: C, 65.8; H, 5.2. $C_{18}H_{16}O_4S$ requires C, 65.8; H, 4.9%); $\nu_{max.}$ (film) 3438, 1747, 1705, 1673, 1311, 1231, 1100, and 698 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.07 (3 H, t, J 7.2 Hz, $CO_2CH_2CH_3$ hydrate), 1.32 (3 H, t, J 7.2 Hz, $CO_2CH_2CH_3$ keto), 3.78 (2 H, s, $CH_2Ph$ keto), 4.19 (2 H, s, $CH_2Ph$ hydrate), 4.20 (2 H, q, J 7.2 Hz, $CO_2CH_2$ hydrate), 4.39 (2 H, q, J 7.2 Hz, $CO_2CH_2$ keto), 5.29 (2 H, br, OH hydrate), 7.12-7.37 (5 H, m, $CH_2Ph$), 7.38-7.57 (3 H, m), and

7.95-8.06 (1 H, m); m/z (150°C) 328 (M$^+$, 1%), 282 (1), 255 (1), 237 (1), 227 (58), and 91 (100).

Ethyl 4-[(2-Methoxycarbonylphenyl)thio]-2,3-dioxobutanoate [enol form] (**14**).
Dirhodium tetraacetate (2 mg) was added to a solution of (**10**) (68 mg, 0.20 mmol) in benzene (30 ml) which had been rapidly heated to reflux. After 5 min at reflux, the yellow coloured solution was cooled, evaporated, dichloromethane (5 ml) added and the catalyst removed by filtration through Celite. The filtrate was evaporated, and the residue recrystallised to give the title compound (**14**) (32 mg, 51%) as yellow crystals, m.p. 113-117°C (benzene/hexane); (Found: M$^+$, 310.0506. $C_{14}H_{14}O_6S$ requires M, 310.0511); $\nu_{max.}$ (Nujol) 3387, 1715, 1646, 1578, 1562, 1280, 1258, 1167, and 1048 cm$^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.39 (3 H, J 7.1 Hz, $CH_2CH_3$), 3.95 (3 H, s, $CO_2CH_3$), 4.37 (2 H, q, J 7.1 Hz, $CO_2CH_2$), 6.50 (1 H, d, J 2.0 Hz, SCHCOH enol), 7.37 (1 H, ddd, J 7.8, 5.2, 2.0 Hz, ArH), 7.56 (1 H, dt, J 8.0, 1.5 Hz, ArH), 7.59 (1 H, dd, J 7.8, 1.7 Hz, ArH), 7.62 (1 H, d, J 1.7 Hz, CHSAr enol), and 7.97 (1 H, dd, J 7.0, 1.5 Hz, ArH); m/z (150°C) 310 (M$^+$, 54%), 279 (4), 209 (24), 181 (100), 167 (45), 136 (26),and 45 (86).

Ethyl 3-(t-Butyldimethylsiloxy)-4-[(2-methoxycarbonylphenyl)thio]-2-oxobut-3-enoate.
Triethylamine (10 µl, 71 µmol) and t butyldimethylsilyl trifluoromethanesulphonate (15.1 µl, 66 µmol) were added to a solution of (**14**) (17.0 mg, 55 µmol) in THF (1 ml), and the solution stirred for 6 h at room temperature, before evaporation of the solvent, and rapid chromatography of the residue on Florisil to give the title compound (16 mg, 69%) as a yellow oil; (Found: M$^+$, 409.1141. $C_{20}H_{28}O_6SSi$ - $CH_3$ requires M, 409.1141); $\nu_{max.}$ (film) 1724, 1666, 1557, 1354, 1288, 1256, and, 1061 cm$^{-1}$; $\delta_H$ (270 MHz; $CDCl_3$) 0.25 (6 H, s ), 1.03 (9 H, s), 1.36 (3 H, t, J 7.0 Hz, $CH_2CH_3$), 3.93 (3 H, s, $CO_2CH_3$), 4.33 (2 H, q, J 7.0 Hz, $CO_2CH_2$), 7.30-7.40 (1 H, m), 7.48-7.63 (3 H, m), and 7.94 (1 H, d, J 7.0 Hz); m/z (130°C) 424 (M$^+$, 1%), 409 (3), 393 (1), 367 (100), 235 (30), 167 (46), 136 (45), 73 (44).

***Reactions of Cyclic Sulphoxonium Ylides***

Ethyl 3-oxo-2-allylthiane-1-oxide-2-carboxylate (**16**).
A solution of (**17**) (57.5 mg, 0.225 mmol) in dichloromethane (2 ml) was treated with m-CPBA (58 mg) at 15°C. The reaction mixture was subjected to reductive

work-up and chromatographic purification, to give the title compound (**16**) as a viscous oil (38 mg, 62%), b.p. 130°C at 0.4 mmHg; (Found: C, 54.1; H, 6.7. $C_{11}H_{16}O_4S$ requires C, 54.1; H, 6.6%); $\nu_{max.}$ (film) 1728, 1713, 1641, 1299, 1219, and 1054 $cm^{-1}$; $\delta_H$ (270 MHz; $CDCl_3$) 1.25 (3 H, t, J 6.0 Hz), 2.20-2.34 (1 H, m), 2.46-2.66 (2 H, m), 2.70-3.00 (3 H, m), 3.05-3.29 (2 H, m), 4.23 (2 H, dq, J 6.0, 2.0 Hz), 5.12-5.29 (2 H, m), and 5.65-5.85 (1 H, m); m/z (140°C) 244 ($M^+$, 74%), 228 (2), 216 (6), 198 (25), 187 (7), 181 (57), 176 (34), 171 (7), 118 (54), 90 (92), and 41 (100).

Ethyl 3-Hydroxybenzo[b]thiophene-2-carboxylate (**18**).
A solution of (**12b**) (150 mg, 0.45 mmol) in ethanol (100 ml) under nitrogen was irradiated (254 nm) for 1.25 h. The solvent was evaporated and the residue purified by chromatography to give the title compound (**18**) (31 mg, 31%) as low melting crystals, m.p. 52-55°C, lit.,[9] m.p. 74°C; $\nu_{max.}$ (melt) 3113, 1715, 1658, 1577, 1536, 1401, 1378, 1342, 1307, 1237, 1148, 758, and 733 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.42 (3 H, t, J 7.0 Hz, $CH_2CH_3$), 4.43 (2 H, q, J 7.0 Hz, $CH_2CH_3$), 7.40 (1 H, dt, J 7.1, 1.5 Hz), 7.50 (1 H, dt, J 7.3, 1.5 Hz), 7.74 (1 H, approx d, J 8.1 Hz), 7.94 (1 H, approx d, J 6.8 Hz), and 10.20 (1 H, br, OH); m/z (100°C) 222 ($M^+$, 33), 176 (100), 148 (2), 120 (25), 104 (6), and 77 (7).

Ethyl 3-Acetoxybenzo[b]thiophene-2-carboxylate (**19**).
Acetic anhydride (7.4 µl, 78 µmol) and pyridine (26 µl, 0.30 mmol) were added to a solution of (**18**) (14.5 mg, 65 µmol) in dichloromethane (0.5 ml). The solution was stirred for 12 h and evaporated under high vacuum. The crude product was recrystallised to give the title compound (**19**) as colourless crystals, m.p. 104-105°C, lit.,[10] m.p. 105°C; $\nu_{max.}$ (Nujol) 1706, 1535, 1280, 1249, 1186, 1061, and 737 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 1.38 (3 H, t, J 7.0 Hz, $CH_2CH_3$), 2.47 (3 H, s, COMe), 4.36 (2 H, q, J 7.0 Hz, $CH_2CH_3$), 7.42 ( 1 H, m), 7.50 (1 H, dt, J 7.5, 1.5 Hz), 7.71 (1 H, dt, J 8.5, 1.1 Hz), and 7.80 (1 H, m); m/z (100°C) 264 ($M^+$, 6%), 222 (51), 176 (100), 120 (16), 104 (5), 76 (5), and 43 (13).

2,3-Dihydro-3-oxo-1-phenylbenzo[b]thiophene-1-oxide-2-carboxylic acid , inner salt (**20**).
A solution of potassium hydroxide (0.38 g, 6.8 mmol) in water (5 ml) was added to a solution of (**12a**) (215 mg, 0.684 mmol) in ethanol (8 ml) and the solution stirred at room temperature for 15 h, and then heated at reflux for 1 h. Work-up and recrystallisation of the crude product gave the title compound (**20**) (114 mg, 58%) as colourless crystals, m.p. 174-178°C (dec.) (ethyl acetate/ methanol); (Found: C,

62.7; H, 3.6. $C_{15}H_{10}O_4S$ requires C, 62.9; H, 3.5%); $\nu_{max.}$ (Nujol) 3400-2200, 1720, 1689, 1619, 1448, 1382, 1219, and 1110 $cm^{-1}$; $\delta_H$ (250 MHz; $d_6$-DMSO) 7.67-7.76 (2 H, m), 7.77-7.88 (2 H, m), 7.90-7.97 (2 H, m), 7.97-8.05 (3 H, m), and 10.92 (1 H, br, $CO_2H$); m/z (150°C) 286 ($M^+$, 16%), 242 (33), 213 (8), 197 (19), 184 (9), 165 (28), 136 (100), 108 (22), 77 (32), and 44 (58).

2,3-Dihydro-3-oxo-1-phenylbenzo[b]thiophene-1-oxide, inner salt (**21**).
A solution of (**20**) (114 mg, 0.40 mmol) and acetic acid (0.2 ml) in xylene (7 ml) was heated at reflux for 1.25 h. The solvent was evaporated, and the residue subjected to chromatography on silica gel to give the title compound (**21**) (85 mg, 88%) as yellow crystals, m.p. 165-167°C (ether/hexane); (Found: C, 69.2; H, 4.1. $C_{14}H_{10}O_2S$ requires C, 69.4; H, 4.1%); $\nu_{max.}$ (Nujol) 1631, 1605, 1510, 1277, and 1224 $cm^{-1}$; $\delta_H$ (250 MHz; $CDCl_3$) 4.77 (1 H, br, SCH), 7.50-7.75 (6 H, m), 7.87-7.94 (1 H, m), and 8.00-8.08 (2 H, m); m/z (100°C) 242 ($M^+$, 41%), 213 (47), 184 (20), 165 (19), 136 (100), 108 (21), and 77 (22).

## ACKNOWLEDGEMENTS

We thank the S.E.R.C. for a studentship (to R.J.T.), and the Royal Society of Chemistry for a Hickinbottom Fellowship (to C.J.M.).

## REFERENCES AND NOTES

1. Part 5, C. J. Moody and R. J. Taylor, *Tetrahedron*, preceding paper.
2. P. D. Kennewell and J. B. Taylor, *Chem. Soc. Rev.*, 1975, **4**, 189.
3. (a) J. Diekmann, *J. Org. Chem.*, 1965, **30**, 2272.
   (b) W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, 1969, 1979.
   (c) F. Dost and J. Gosselck, *Chem. Ber.*, 1972, **105**, 948.
   (d) W. Ando, *Acc. Chem. Res.*, 1977, **10**, 179.
4. J. C. Dyer and S. A. Evans, *J. Org. Chem.*, 1980, **45**, 5350.
5. Preliminary communication:
   C. J. Moody, A. M. Z. Slawin, R. J. Taylor, and D. J. Williams, *Tetrahedron Lett.*, 1988, **29**, 6009.

6. Cyclic sulphoxonium ylides are rare, although a few examples have been prepared from dimethylsulphoxonium methylide: (a) E. J. Corey and M. Chaykovsky, *Tetrahedron Lett.*, 1963, 169; (b) *J. Am. Chem. Soc.*, 1964, **86**, 1640; (c) A. Burger, M. Bernabe, and P. W. Collins, *J. Med. Chem.*, 1970, **13**, 33.
7. R. Pellicari, B. Natalini, S. Cecchetti, and R. Fringuelli, *J. Chem. Soc., Perkin Trans. 1*, 1985, 493.
U. Schollkopf, B. Banhidai, H. Frasnelli, R. Meyer, and H. Beckhaus, *Liebigs Ann. Chem.*, 1974, 1767.
8. The *X*-ray structures for compounds (**11c**), (**12a**), and (**14**) and crystal data are given in our preliminary communication (reference 5).
9. F. Arndt and P. Nachtwey, *Chem. Ber.*, 1916, **59**, 1073.
10. E. W. McClelland, M. J. Rose, and D. W. Stammers, *J. Chem. Soc.*, 1948, 81.
11. C. J. Moody and R. J. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1989, 721.
12. J. C. Heslin and C. J. Moody, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1417.