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RHODIUM CARBENOID MEDIATED CYCLISATIONS. PART 5.[1] SYNTHESIS AND REARRANGEMENT OF CYCLIC SULPHONIUM YLIDES; PREPARATION OF 6- AND 7-MEMBERED SULPHUR HETEROCYCLES

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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 mercaptans with rhodium(II) acetate gives six- and seven-membered sulphur heterocycles; diazo sulphides give cyclic sulphonium ylides, which are isolable, or rearrange, depending on the nature of the substituent on sulphur.

The reaction of electrophilic carbenes and carbenoids with divalent sulphur compounds to give sulphonium ylides is well described,[2-4] and provided that the carbene substituents are electron withdrawing, the ylides are stable and isolable. Stable *cyclic* sulphonium ylides are less well known, although a few have been prepared by treatment of cyclic sulphonium salts with base,[5] rather than by a carbene route. The attempts to effect the intramolecular version of the sulphide-carbene reaction have usually resulted in products arising from rearrangement of a non-isolable cyclic ylide,[2,3] although such reactions have been elegantly used in synthesis.[6] However, the recent work of Davies on the rhodium(II) acetate catalysed decomposition of diazo phenylsulphides has shown that stable 5-,6-, and 7-membered cyclic sulphonium ylides can be formed by the carbenoid route.[7] In continuation of our interest in rhodium carbenoid mediated cyclisations, we have also investigated the reactions of diazo mercaptans and diazo sulphides, and we now report our results in full.[8]

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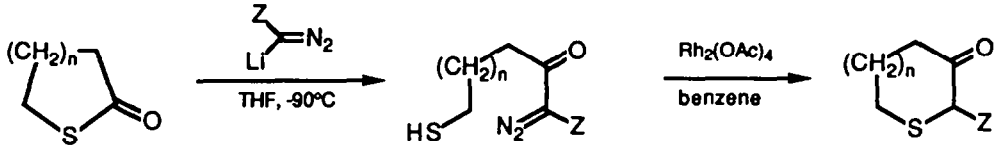
RESULTS AND DISCUSSION

Preparation and Rhodium(II) Catalysed Cyclisation of Diazo Mercaptans

We have previously described the ring opening reactions of lactones with ethyl lithiodiazoacetate (ELDA) as a route to diazo alcohols, substrates for rhodium carbenoid mediated cyclisation to cyclic ethers,[9] and we have recently reported the extension of this reaction to include other lithiated diazo compounds.[10] The reaction of ELDA, generated from ethyl diazoacetate and lithium diisopropylamide (LDA) with γ–thiobutyrolactone and δ-thiovalerolactone at -90°C gave the diazo mercaptans (**2a**) and (**2b**) directly in reasonable yield. The acetyl and phosphonyl diazo mercaptans (**2c**) and (**2d**), however, were formed in poor yield on reaction of the appropriate thiolactone (**1**) with the lithiated derivatives of diazo acetone[11] and diethyl diazomethylphosphonate[12] respectively (Table 1). Reaction of lithiotrimethylsilyldiazomethane with γ-thiobutyrolactone was unsuccessful.

On heating in boiling benzene in the presence of *ca.* 2 mol% rhodium(II) acetate, the diazo mercaptans (**2**) gave the cyclic thioethers (**3**) in modest yield (Table 1). There is only one previous example of an intramolecular reaction between a diazo compound and a mercaptan; methyl 2-diazo-5-mercapto-3-oxopentanoate cyclises to methyl 3-oxotetrahydrothiophene-2-carboxylate on treatment with rhodium acetate.[13] In the present cases, the -SH group seemed to poison the catalyst, which changed from its normal emerald green colour to purple.



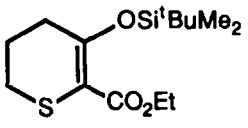
(1) (2) (3)

Table 1. *Preparation and Cyclisation of Diazo Mercaptans*

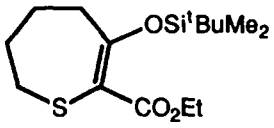
n	Z	Diazo Compound (2)	Yield (2) (%)	Product (3)	Yield (3) (%)
1	CO_2Et	**2a**	44	**3a**	57[a]
2	CO_2Et	**2b**	58	**3b**	34[a]
2	COMe	**2c**	20	**3c**	41[b]
1	$PO(OEt)_2$	**2d**	18	**3d**	44[a]

[a] Exists as a mixture of keto and enol forms; [b] Exists entirely in the enol form.

The cyclic thioethers (**3**) exist as mixtures of keto and enol forms, with the acetyl compound (**3c**) being totally enolised. As further proof of their structures, the thiane and thiepane β-keto esters (**3a**) and (**3b**) were converted into their *t*-butyldimethylsilyl enol ethers (**4**) and (**5**) in quantitative yield by treatment with *t*-butyldimethylsilyl trifluoromethanesulphonate and triethylamine.



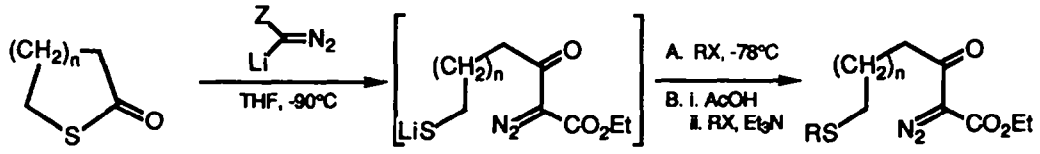
(**4**)



(**5**)

Preparation and Rhodium (II) Catalysed Cyclisation of Diazo Sulphides

The method most widely used to prepare diazo sulphides involves alkylation of a simple thiolate anion with a functionalised alkyl halide, followed by introduction of the diazo group into the molecule. Since we already had developed a route to diazo mercaptans, we were able to use simple alkyl halides to obtain the desired diazo sulphides. Two procedures were used: since the intermediate in the formation of the diazo mercaptans (**2**) is the lithium thiolate (**6**), quenching the reaction mixture with an alkyl halide gave the diazo sulphide directly. Alternatively the diazo mercaptans (**2a**, **2b**) could be isolated, purified, and subsequently alkylated using an alkyl halide in the presence of triethylamine in dimethylformamide (DMF). In practice, however, we found that the best method was to quench the lithium thiolate (**6**) with acetic acid, and to "clean up" the crude diazo mercaptan (**2a**, **2b**) by flash chromatography. This partially purified material was then used in the subsequent alkylation reactions (Table 2). In this way the diazo mercaptan (**2a**) could be alkylated with alkyl halides such as iodoethane and benzyl bromide, and α-chloroketones to give the diazo sulphides (**7a**), (**7b**), and (**7c**). Reaction with allyl, prenyl, and cinnamyl bromides proceeded as expected to give the diazo sulphides (**7d**), (**7e**), and (**7f**) respectively, the cinnamyl derivative (**7f**) being exclusively the (E)-isomer. With crotyl bromide, however, which contains *ca.* 20% 3-bromo-1-butene, three products were obtained (total 52%) which could not be separated by chromatography. The major compound, which accounted for *ca.* 80% of the product, was the derived (E)-but-2-enyl sulphide (**7g**), with the corresponding *Z*-alkene (*ca.* 10%), and the isomeric 1-methylprop-2-enyl sulphide (*ca.* 10%) accounting for the rest. The diazo mercaptan (**2a**) could also be acylated with acetic anhydride or ethyl malonyl chloride. The diazo sulphides (**7j**) and (**7k**) were prepared from the diazo mercaptan (**2b**) by alkylation with benzyl and cinnamyl bromide respectively.



(1) (6) (7)

Table 2 Preparation of Diazo Sulphides

n	RX	(7)	Yield[a] (7) (%)
1	EtI	**a**	60
1	$PhCH_2Br$	**b**	50
1	$EtO_2CCH_2COCH_2Cl$	**c**	34 (60)[b]
1	$H_2C{=}CHCH_2Br$	**d**	55
1	$Me_2C{=}CHCH_2Br$	**e**	37 (54)[c]
1	(E)-$PhCH{=}CHCH_2Br$	**f**	46 (62)[b]
1	(E)-$MeCH{=}CHCH_2Br$	**g**	52[d]
1	$(MeCO)_2O$	**h**	50
1	MeO_2CCH_2COCl	**i**	47
2	$PhCH_2Br$	**j**	31
2	(E)-$PhCH{=}CHCH_2Br$	**k**	48

a Yield refers to alkylation of partially purified diazo mercaptan (method B);

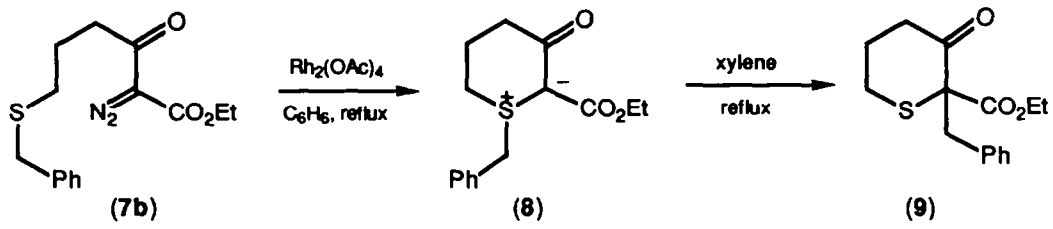
b Yield refers to alkylation of purified diazo mercaptan;

c Yield in brackets refers to Method A;

d See text.

On heating in boiling benzene in the presence of a catalytic amount of rhodium(II) acetate, the diazo sulphide (**7b**) gave the crystalline *S*-benzyl cyclic sulphonium ylide (**8**), m.p. 134-135°C in 24% yield. Although the ylide (**8**) is stable at room temperature, it undergoes a Stevens type [1,2]-rearrangement to give the thiane (**9**) on heating in boiling xylene for 2.5 h. (Scheme 1). No products resulting from alternative rearrangement pathways were detected, and this result contrasts with that obtained from a related *S*-benzyl cyclic ylide, which undergoes a formal [1,4]-rearrangement to the carbonyl oxygen.[14] The diazo benzyl sulphide (**7j**), the homologue of (**7b**), did not give the corresponding 7-membered *S*-benzyl sulphonium

ylide on treatment with rhodium(II) acetate in benzene. Instead, the only product isolated in poor yield was the debenzylated thiepane (**3b**).

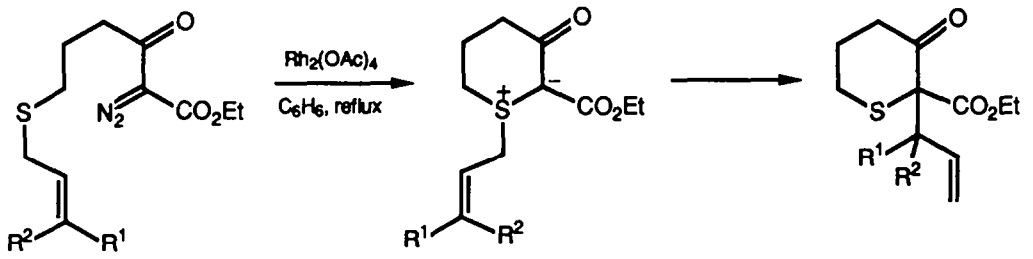


(**7b**) (**8**) (**9**)

Scheme 1

The symmetry-allowed [2,3]-sigmatropic rearrangement of *S*-allyl sulphonium ylides is generally quite facile,[2-4] and because of this, *S*-allyl sulphonium ylides cannot usually be isolated since they rearrange under the conditions of their generation.[15] However, the intramolecular capture of carbenes or carbenoids by allyl sulphides to give cyclic *S*-allyl sulphonium ylides is rare, although the intermolecular reaction is well known.[3] In the present case, we found that rhodium(II) acetate catalysed decomposition of the diazo allylsulphide (**7d**) in boiling benzene gave the rearranged thiopyran (**11a**) (59%) directly. The intermediate cyclic sulphonium ylide (**10**) was not detected. That the thiopyran (**11a**) was formed by a [2,3]-rearrangement rather than by a [1,2]-shift of the allyl group was shown by the formation, with allylic inversion, of the thiopyrans (**11b**) (66%), (**11c**) (78%), and (**11d**) (71%) from the *S*-prenyl (**7e**), *S*-cinnamyl (**7f**), and *S*-crotyl (**7g**) diazo compounds respectively (Scheme 2). The thiopyrans (**11c**) and (**11d**) were formed as mixtures of diastereoisomers, approximately 3:2 and 2:1 respectively, and, of course, the decomposition of the diazo sulphide (**7g**) was further complicated by the presence of the minor isomers referred to above. However, the total product distribution observed from diazo compound (**7g**) was consistent with that expected from a [2,3]-sigmatropic rearrangement of all the isomers.

The formation and rearrangement of cyclic *S*-allyl sulphonium ylides was also extended to 7-membered rings. Thus decomposition of the diazo sulphide (**7k**) under the usual conditions gave the cyclic sulphide (**13**) in low yield (26%), presumably *via* the 7-membered ring *S*-ylide (**12**) (Scheme 3). In this case the [2,3]-sigmatropic rearrangement supervenes over the facile ring fragmentation by elimination of the β-hydrogen that occurs with the corresponding 7-membered *S*-phenyl ylide.[7]

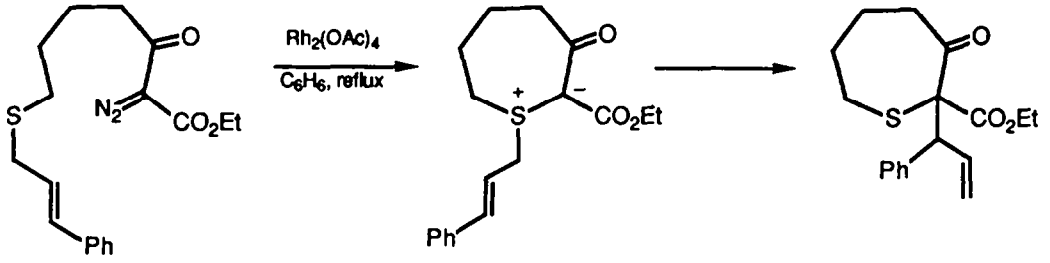


(7) (10) (11)

d, $R^1 = R^2 = H$
e, $R^1 = R^2 = Me$
f, $R^1 = Ph$, $R^2 = H$
g, $R^1 = Me$, $R^2 = H$

a, $R^1 = R^2 = H$
b, $R^1 = R^2 = Me$
c, $R^1 = Ph$, $R^2 = H$
d, $R^1 = Me$, $R^2 = H$

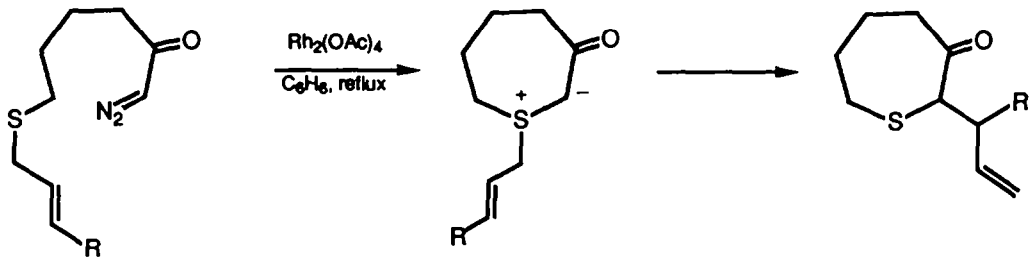
Scheme 2



(7k) (12) (13)

Scheme 3

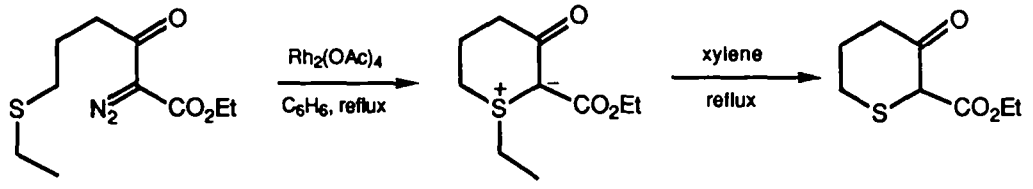
Since the yield of the 7-membered ring sulphide (**13**) was low, we also investigated the cyclisation of the diazo sulphides (**14**). These were prepared from 5-mercaptopentanoic acid[16] by *S*-alkylation, conversion into the acid chloride, and reaction with diazomethane. Rhodium(II) acetate catalysed decomposition of the diazo sulphides (**14a**) and (**14b**) gave the rearranged cyclic sulphides (**15a**) and (**15b**) in 42 and 64% yield respectively (Scheme 4). The thiepane (**15b**) was formed as a mixture of diastereoisomers (ratio *ca.* 4:1).



(14) (15)

Scheme 4 [**a**, R = H; **b**, R = Ph]

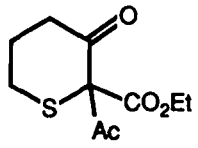
In addition to [1,2]- and [2,3]-rearrangements, the other major reaction pathway for acyclic sulphonium ylides is β-elimination,[2] and since we did not observe elimination reactions involving the *endocyclic* β-hydrogen atoms of our cyclic ylides, we investigated the preparation of ylides containing *exocyclic* β-hydrogens. Decomposition of the *S*-ethyl diazo sulphide (**7a**) in boiling benzene in the presence of rhodium(II) acetate gave the ylide (**16**) (Scheme 5), which on further heating in xylene underwent β-elimination of ethylene to give the thiopyran (**3a**). Alternatively heating the diazo compound (**7a**) and rhodium(II) acetate in boiling xylene gave (**3a**) directly in 88% yield.



(7a) (16) (3a)

Scheme 5

The thiopyran (**3a**) was also formed in low yield on decomposition of the *S*-acyl diazo compound (**7i**). In this case the malonyl group in the intermediate ylide is presumably eliminated as ethoxycarbonylketene. In contrast, decomposition of the *S*-acetyl diazo compound (**7h**) did not result in elimination of ketene; rather, the intermediate underwent [1,2]-rearrangement of the acetyl group to give the thiopyran (**17**) in 40% yield.



(17)

CONCLUSIONS

The rhodium(II) acetate catalysed cyclisation reactions of 1,5- and 1,6-diazo sulphides provides a route to substituted thianes and thiepanes by way of cyclic sulphonium ylides, which in some cases may be isolated. The reactions involve the intramolecular interception of rhodium carbenoids by sulphides; the formation of cyclic sulphoxonium ylides by the corresponding reactions of sulphoxides is described in the following paper.

EXPERIMENTAL

For general points see refs. 9 and 17.

Preparation of Diazomercaptans (2)

Ethyl 2-Diazo-6-mercapto-3-oxohexanoate (**2a**).
Ethyl diazoacetate (2.34 ml, 22.3 mmol) was added dropwise to a solution of LDA (21.6 mmol) in THF (40 ml) over 10 min at -90°C. The orange solution was stirred for 10 min, and γ-thiobutyrolactone (Aldrich) (1.77 ml, 20.6 mmol) added over a period of 15 min. The solution was stirred for 0.5 h at -90°C, and then 0.5 h at –75°C before the addition of acetic acid (1.8 ml). Work-up and chromatography on acidic alumina gave the title compound (**2a**) (1.97 g, 44%) as a yellow oil. (Found: C, 44.4; H, 5.6. $C_8H_{12}N_2O_3S$ requires C, 44.4; H, 5.6%); $\nu_{max.}$ (film) 2572, 2137, 1717, 1655, and 1306 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.30 (3 H, t, J 7.2 Hz, $CH_2\underline{Me}$), 1.33 (1 H, t, J 8.1 Hz, SH), 1.92 (2 H, quin, J 7.1 Hz, $CH_2\underline{CH_2}CH_2$), 2.56 (2 H, q, J 7.4 Hz, $\underline{CH_2}SH$), 2.95 (2 H, t, J 7.2 Hz, $\underline{CH_2}CO$), and 4.27 (2 H, q, J 7.1 Hz, $\underline{CH_2}Me$); m/z (FAB) 217 ($\underline{M}H^+$); m/z (140°C) 188 ($\underline{M}^+ - N_2$, 4%), 171 (2), 169 (3), 156 (29), and 142 (100).

Ethyl 2-Diazo-7-mercapto-3-oxoheptanoate (**2b**).
Ethyl diazoacetate (0.43 ml, 4.1 mmol) was added dropwise to a solution of LDA (4.1 mmol) in THF (20 ml) at -92°C over a period of 12 min. After 15 min the solution was cooled to -95°C and δ-thiovalerolactone[16] (453 mg, 3.90 mmol) in THF (2 ml) added dropwise over 12 min. The solution was stirred at -92°C for 0.5 h, and then at -75°C for 3 h before the addition of acetic acid (0.66 ml). Work-up and chromatography gave the title compound (**2b**) (522 mg, 58%) as a yellow oil; (Found: C, 47.2; H, 6.2; N, 12.3; S, 13.5. $C_9H_{14}N_2O_3S$ requires C, 46.9; H, 6.1; N, 12.2; S, 13.9%); $\nu_{max.}$ (film) 2572, 2136, 1718, 1656, and 1306 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.1-1.4 (4 H, m, CH_2Me and SH), 1.40-2.05 (4 H, m), 2.52 (2 H, q, J 6.6 Hz, CH_2SH), 2.83 (2 H, t, J 6.5 Hz, CH_2CO), and 4.28 (2 H, q, J 6.9 Hz, CH_2Me); m/z (FAB; glycerol) 231 (MH^+, 7%), 197 (18), and 169 (21).

3-Diazo-8-mercapto-octane-2,4-dione (**2c**).
Diazoacetone (177 mg, 2.10 mmol) was added dropwise to a solution of LDA (2.10 mmol) in THF (6 ml) at -90°C. After 5 min, δ-thiovalerolactone (232 mg, 2.00 mmol) was added dropwise, and after a further 5 min, the reaction was warmed to –75°C, and the temperature maintained for 2 h. Acetic acid (0.3 ml) was added , and the mixture warmed to -20°C, then water was added, followed by work-up and purification by chromatography to give δ-thiovalerolactone (44 mg,19%) and the title compound (**2c**) (78 mg, 20%) as a yellow oil; (Found: M^+, 172.0555. $C_8H_{12}N_2O_2S$-N_2 requires M, 172.0558); $\nu_{max.}$ (film) 2570, 2123, 1666, 1365, 1298, and 1224 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.31 (1 H, t, J 7.8 Hz, SH), 1.51-1.77 (4 H, m, $CH_2CH_2CH_2$), 2.37 (3 H, s, COMe), 2.48 (2 H, q, J 7.1 Hz, CH_2S), and 2.69 (2 H, t, J 6.9 Hz, CH_2CO); m/z (90°C) 172 (M^+-N_2, 5%), 167 (3), 154 (7), 139 (5), 85 (46), and 43 (100).

Diethyl (1-Diazo-5-mercapto-2-oxopentyl)phosphonate (**2d**).
n-Butyllithium (0.47 ml, 0.73 mmol) was added dropwise to a solution of diethyl diazomethylphosphonate (130 mg, 0.73 mmol) in THF (5 ml) at -75°C. After 15 min, γ–thiobutyrolactone (74 mg, 0.73 mmol) was added dropwise. The reaction mixture was stirred for 3 h and allowed to warm to -30°C over 1 h before the addition of acetic acid (0.1 ml). Aqueous work-up and chromatography gave the title compound (**2d**) (36 mg, 18%) as a yellow oil; (Found: M^+, 252.0592. $C_9H_{17}N_2O_4PS$ - N_2 requires M, 252.0585); $\nu_{max.}$ (film) 2547, 2122, 1656, 1262, and 1018 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.27 (1 H, t, J 7.1 Hz, SH), 1.33 (6 H, dt, J 7.0, 0.9 Hz, CH_2CH_3), 1.89 (2 H, quin, J 7.1 Hz, CH_2CH_2S), 2.52 (2 H, q, J 7.2 Hz, CH_2S), 2.65 (2 H, t, J 6.8 Hz, CH_2CO),

and 4.04-4.26 (4 H, m, OCH_2); m/z (120°C) 252 (M^+-N_2, 100%), 234 (5), 224 (35), 219 (27), 196 (60), 178 (57), and 98 (92).

Rhodium Carbenoid Mediated Cyclisation of Diazomercaptans

Ethyl 3-Oxothiane-2-carboxylate (**3a**).
A solution of (**2a**) (120 mg, 0.556 mmol) in benzene (5 ml) was added to a suspension of dirhodium tetraacetate (4 mg) in benzene (15 ml) at reflux over 5 min. After 10 min at reflux the pale purple solution was cooled, evaporated, and the residue subjected to chromatography to give the title compound (**3a**) (59 mg, 57%) as a clear oil; b.p. 130-140°C at 0.4 mmHg; (Found: C, 51.1; H, 6.7. $C_8H_{12}O_3S$ requires C, 51.0; H, 6.4%); $\nu_{max.}$ (film) 1745, 1719, 1651, 1603, 1380, 1297 and 1219 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.29 (3 H, t, J 7.0 Hz, CH_2CH_3, keto), 1.32 (3 H, t, J 7.0 Hz, CH_2CH_3, enol), 2.10 (2 H, m, $CH_2CH_2CH_2$, keto/enol), 2.40 (2 H, approx t, J 6.5 Hz, CH_2S, enol), 2.40-2.64 (2 H, m, CH_2S, keto), 2.78 (2 H, approx t, J 5.6 Hz, CH_2CO, enol), 2.80-3.14 (2 H, m, CH_2CO, keto), 3.95 (1 H, s, COCHS, keto), 4.23 (2 H, q, J 7.0 Hz, CO_2CH_2, keto), 4.24 (2 H, q, J 7.0 Hz, CO_2CH_2, enol), and 10.48 (1 H, s, OH, enol); *ca.* 75% enol form; m/z (110°C) 188 (M^+, 56%), 142 (100), 115 (18), 86 (41), and 69 (21).

Ethyl 3-Oxothiepane-2-carboxylate (**3b**).
A solution of (**2b**) (462 mg, 2.01 mmol) in benzene (10 ml) was added over 1 h to a stirred suspension of dirhodium tetraacetate (2.9 mg) in benzene (40 ml) at reflux. After 0.5 h, extra catalyst (3 mg) was added. Reflux was continued for 2 h, before the mixture was cooled, evaporated and the residue purified by chromatography to give the title compound (**3b**) (138 mg, 34%) as a clear oil; (Found: C, 53.7; H, 7.2. $C_9H_{14}O_3S$ requires C, 53.4; H, 7.0%. Found: M^+, 202.0663; requires M, 202.0664); $\nu_{max.}$ (film) 1742, 1707, 1632, 1595, 1377, 1308, and 1242 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.24 (3 H, t, J 7.0 Hz, CH_2CH_3, keto), 1.29 (3 H, t, J 7.0 Hz, CH_2CH_3, enol), 1.56-2.05 (4 H, m, $CH_2CH_2CH_2S$, keto/enol), 2.54 (2 H, approx t, J 5.5 Hz, CH_2S, enol), 2.68 (2+2 H, m, CH_2S keto, and CH_2CO keto/enol), 4.22 (1 H, s, COCHS, keto), 4.23 (2 H, q, J 7.1 Hz, CO_2CH_2, keto), 4.26 (2 H, q, J 7.1 Hz, CO_2CH_2, enol), and 9.63 (1 H, s, OH, enol); *ca.* 65% enol; m/z (180°C) 202 (M^+, 61%), 169 (6), 156 (80), 128 (33), 100 (13), 87 (100).

2-Acetylthiepan-3-one [enol form] (**3c**).
As solution of (**2c**) (56.8 mg, 0.285 mmol) in benzene (5 ml) was added dropwise to a suspension of dirhodium tetraacetate (3 mg) in benzene (15 ml) at reflux over 3 min. After 2 min at reflux, the reaction mixture was cooled, filtered and evaporated. The residue was subjected to chromatography to give the title compound (**3c**) (20 mg, 41%) as a low melting solid, m.p. 38-40°C, b.p. 120-130°C at 0.25 mmHg; (Found: C, 56.0; H, 7.0. $C_8H_{12}O_2S$ requires C, 55.8; H, 7.0%); $\nu_{max.}$ (film) 2750, 1592, 1435, 1293, 983, and 904 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.53-1.87 (2 H, m,), 2.02 (2 H, approx. quin, J 5.6 Hz), 2.36 (3 H, s, COMe), 2.60 (2 H, dd, J 5.4, 4.5 Hz, CH_2CO), 2.92 (2 H, d, J 10.3 Hz, CH_2S), and 14.21 (1 H, s, OH); m/z (130°C) 172 (M^+, 11%), 57 (100), and 41 (66).

Diethyl 3-oxothiane-2-phosphonate (**3d**).
A solution of (**2d**) (34.5 mg, 0.123 mmol) in benzene (6 ml) was rapidly heated to reflux. Dirhodium tetraacetate (1 mg) was added and reflux continued for 5 min. Extra catalyst (2 mg) was added, and reflux maintained for 15 min. The reaction mixture was cooled, evaporated, and the residue purified by chromatography to give the title compound (**3d**) (13.7 mg, 44%) as a clear oil; (Found: C, 43.0; H, 6.9. $C_9H_{17}O_4PS$ requires C, 42.9; H 6.8%); $\nu_{max.}$ (film) 3484, 1712, 1601, 1250, 1048, 1022, and 973 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.30 (3 H, t, J 7.1 Hz , CH_2CH_3), 1.36 (3 H, t, J 7.1 Hz, CH_2CH_3), 2.10-2.60 (4 H, m), 2.73-2.95 (2+1 H, m, CH_2S enol, and HCHS keto), 3.41 (1 H, d, J 20.7 Hz, CHP, keto), 3.65 (1 H, t, J 10.3 Hz, CHS, keto), 4.11 (2 H, dq , J 7.8, 7.0 Hz, OCH_2), 4.30 (2 H, dq , J 7.8, 7.0 Hz, OCH_2), and 10.98 (1H, br, OH, enol); *ca.* 18% enol form; m/z (100°C) 252 (M^+, 100%), 224 (18), 219 (35), 207 (7), 196 (32), 178 (25), 163 (14), 139 (18), 115 (20), 98 (43), and 86 (47).

Ethyl 3-t-Butyldimethylsiloxy-4,5-dihydrothiin-2-carboxylate (**4**).
Triethylamine (48 µl, 0.346 mmol) and t-butyldimethylsilyl triflate (64 µl, 0.277 mmol) were added to a solution of (**3a**) (26 mg, 0.138 mmol) in THF (1 ml) and the mixture stirred overnight. Aqueous work-up with 5% sodium bicarbonate solution and distillation of the crude product gave the title compound (**4**) (42 mg, 100%) as a clear oil, b.p. 150-160°C at 0.2 mmHg; (Found: C, 55.4; H, 8.7. $C_{14}H_{26}O_3SSi$ requires C, 55.6; H, 8.7%); $\nu_{max.}$ (film) 1720, 1688, 1591, 1262, 1200, and 831 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 0.16 (6 H, s), 0.93 (9 H, s), 1.28 (3 H, t, J 7.1 Hz, CH_2CH_3), 2.02-2.15 (2 H, m, CH_2CH_2S), 2.27 (2 H, t, J 6.0 Hz, CH_2COSi), 2.78-2.70 (2 H, m, CH_2S), and 4.18 (2 H, q, J 7.1 Hz, CO_2CH_2); m/z (170°C) 302 (M^+, 5%), 257 (12), 245 (66), 217 (100), and 75 (38).

Ethyl 3-t-Butyldimethylsiloxy-4,5,6,7-tetrahydrothiepin-2-carboxylate (**5**).
Triethylamine (33 μl, 0.232 mmol) and t-butyldimethylsilyl triflate (43 μl, 0.186 mmol) were added to a solution of (**3b**) (18.8 mg, 93 μmol) in ether (1 ml) and the mixture stirred overnight. Aqueous work-up with 5% sodium bicarbonate solution and distillation of the crude product gave the title compound (**5**) (29.6 mg, 100%) as a clear oil, b.p. 160°C at 0.25 mmHg; (Found: C, 57.0; H, 9.0. $C_{15}H_{28}O_3SSi$ requires C, 56.9; H, 8.9%); $\nu_{max.}$ (film) 1714, 1573, 1283, 1207, and 831 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 0.08 (6 H, s), 0.93 (9 H, s), 1.27 (3 H, t, J 7.1 Hz, CH_2CH_3), 1.51-1.63 (2 H, m, $(CH_2)_2CH_2S$), 1.91-2.02 (2 H, m, $(CH_2)_2CH_2S$), 2.58-2.66 (2 H, m, CH_2COSi), 2.73-2.81 (2 H, m, CH_2S), and 4.16 (2 H, q, J 7.1 Hz, CO_2CH_2); m/z (170°C) 316 (M^+, 2%), 301 (2), 271 (11), 259 (79), 231 (100), 145 (9), and 75 (43).

Preparation of Diazosulphides (7)

General procedure for the alkylation of ethyl 2-diazo-6-mercapto-3-oxohexanoate (**2a**) and ethyl 2-diazo-7-mercapto-3-oxoheptanoate (**2b**)

Crude ethyl 2-diazo-6-mercapto-3-oxohexanoate (**2a**) or ethyl 2-diazo-7-mercapto-3-oxoheptanoate (**2b**) (0.5-1 mmol) in DMF (1-2 ml), under an atmosphere of nitrogen, was treated with triethylamine (1.3-1.5 eq) and alkylating agent (1.1-1.3 eq) in succession. After stirring for 12 h at room temperature, the reaction mixture was extracted into dichloromethane and the organic phase was washed with water. The dichloromethane solution was dried over $MgSO_4$, evaporated, and the residue subjected to chromatography to give the diazosulphide.

Ethyl 2-Diazo-6-ethylthio-3-oxohexanoate (**7a**).
Treatment of a solution of crude (**2a**) (250 mg, 1.16 mmol) in DMF (2 ml) with triethylamine (0.21 ml, 1.50 mmol) and ethyl iodide (0.10 ml, 1.28 mmol) gave the title compound (**7a**) (169 mg, 60%) as a yellow oil; (Found: M^+, 216.0815. $C_{10}H_{16}N_2O_3S$ requires M, 216.0820); $\nu_{max.}$ (film) 2135, 1718, 1656, and 1303 cm^{-1}; δ_H (270 MHz; $CDCl_3$). 1.23 (3 H, t, J 6.6 Hz, SCH_2CH_3), 1.31 (3 H, t, J 6.4 Hz, $CO_2CH_2CH_3$), 1.93 (2 H, quin, J 6.3 Hz, CH_2CH_2), 2.52 (2 H, q, J 6.8 Hz, SCH_2Me), 2.56 (2 H, q, J 6.5 Hz, CH_2CH_2S), 2.97 (2 H, m, $COCH_2$), and 4.29 (2 H, q, J 6.5 Hz, CO_2CH_2); m/z (130°C) 244 (M^+, 1%), 216 (31), 187 (33), 170 (3), 156 (18), 142 (23), and 109 (100).

Ethyl 6-Benzylthio-2-diazo-3-oxohexanoate (**7b**).
Treatment of a solution of crude (**2a**) (250 mg, 1.16 mmol) in DMF (2 ml) with triethylamine (0.20 ml, 1.50 mmol) and benzyl bromide (0.146 ml, 1.22 mmol) gave the title compound (**7b**) (179 mg, 50%) as a yellow oil; (Found: C, 59.1; H, 6.3; N, 9.0; S, 10.6. $C_{15}H_{18}N_2O_3S$ requires C, 58.8; H, 5.9; N, 9.2; S, 10.5%); $\nu_{max.}$.(film) 2135, 1718, 1655, 1374, 1303, and 1222 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.31 (3 H, t, J 7 Hz, CH_2CH_3), 1.90 (2 H, quin, J 7 Hz), 2.48 (2 H, t, J 7 Hz, CH_2S), 2.95 (2 H, t, J 7 Hz, CH_2CO), 3.70 (2 H, s, CH_2Ph), 4.30 (2 H, q, J 7 Hz, CO_2CH_2), and 7.30 (5 H, m, ArH); m/z (80°C) 306 (M^+, 1%), 278 (4), 232 (7), 204 (5), 187 (7), and 91 (100).

Ethyl 2-diazo-6-[(3-ethoxycarbonyl-2-oxopropyl)thio]-3-oxohexanoate (**7c**).
Ethyl 4-chloroacetoacetate (0.24 ml, 1.80 mmol) was added to a solution of the pure diazomercaptan (**2a**) (355 mg, 1.64 mmol) and triethylamine (0.25 ml, 1.80 mmol) in DMF at 0°C. After 12 h at -5°C, the reaction mixture was subjected to aqueous work-up, and the residue was purified by chromatography, to give the title compound (**7c**) (339 mg, 60%), as an oil; (Found: C, 49.1; H, 6.0; N, 8.0. $C_{14}H_{20}N_2O_6S$ requires C, 48.8; H, 5.9; N, 8.1%); $\nu_{max.}$ (film) 2137, 1744, 1718, 1655, and 1304 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.25 (3 H, t, J 7.0 Hz, CH_2Me), 1.30 (3 H, t, J 7.1 Hz, CH_2Me), 1.90 (2 H, quin, J 6.9 Hz, CH_2CH_2S), 2.51 (2 H, t, J 7.1 Hz, CH_2COCN), 2.92 (2 H, t, J 7.2 Hz, CH_2S), 3.34 (2 H, s, $COCH_2S$), 3.64 (2 H, s, $COCH_2CO$), 4.18 (2 H, q, J , 7.0 Hz, CH_2Me), and 4.27 (2 H, q, J , 6.9 Hz, CH_2Me); m/z (100°C) 344 (M^+,1%), 306 (1), 292 (1), 278 (2), 205 (6), 159 (9), 57 (25), 43 (35) and 28 (100).

Ethyl 6-Allylthio-2-diazo-3-oxohexanoate (**7d**).
A solution of crude (**2a**) (117 mg, 0.541 mmol) in THF (1.5 ml) was treated with triethylamine (0.10 ml, 0.76 mmol) and allyl bromide (100 mg, 1 mmol). After 12 h, work-up and purification gave the title compound (**7d**) (76 mg, 55%) as a pale yellow liquid; (Found: C, 51.4; H, 6.3; N, 11.0; S, 12.7. $C_{11}H_{16}N_2O_3S$ requires C, 51.4; H, 6.3; N, 10.9; S, 12.5%); $\nu_{max.}$ (film) 2136, 1718, 1657, and 1303 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.27 (3 H, t, J 7.2 Hz, CH_2CH_3), 1.85 (2 H, quin, J 7.2 Hz, CH_2CH_2S), 2.45 (2 H, t, J 7.2 Hz, CH_2CH_2S), 2.90 (2 H, t, J 7.2 Hz, CH_2CO), 3.07 (2 H, d, J 7.0 Hz, $CHCH_2S$), 4.24 (2 H, q, J 7.2 Hz, CO_2CH_2), 4.98-5.09 (2 H, m, $CH{:}CH_2$), and 5.71 (1 H, ddt, J 16.5, 10.0, 7.1 Hz, $CH_2{:}CH$); m/z (80°C) 256 (M^+, 12%), 228 (6), 211 (4), 187 (49), 169 (9), 155 (12), 113 (23), 109 (71), 41 (100).

Ethyl 2-Diazo-6-(3-methylbut-2-enyl)thio-3-oxohexanoate (**7e**).
A solution of crude (**2a**) (500 mg, 2.32 mmol) in DMF (4 ml) was treated with triethylamine (0.50 ml, 5.0 mmol) and prenyl bromide (0.346 g, 4.00 mmol), to give the title compound (**7e**) (246 mg, 37%) as a yellow oil; (Found: C, 55.1; H, 7.5; N, 10.1. $C_{13}H_{20}N_2O_3S$ requires C, 54.9; H, 7.1; N, 9.9%. Found: M$^+$, 256.1132; requires M-N_2, 256.1133); $\nu_{max.}$ (film) 2135, 1718, 1657, 1375, 1303, and 1221 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.26 (3 H, t, J 7.0 Hz, CH_2CH_3), 1.58 (3 H, s, Me), 1.66 (3 H, s, Me), 1.85 (2 H, quin, J 7.0 Hz, $CH_2CH_2CH_2$), 2.45 (2 H, t , J 7.0 Hz, CH_2S), 2.90 (2 H, t , J 7.0 Hz, CH_2CO), 3.06 (2 H, d , J 7.6 Hz, $CHCH_2S$), 4.23 (2 H, q, J 6.9 Hz, CO_2CH_2), and 5.25 (1 H, t quin, J 7.6, 1.4 Hz, CHCMe); m/z (100°C) 284 (M$^+$, 1%), 256 (9), 210 (6), 195 (5), 188 (13), 155 (5), 142 (34), 69 (100), and 41 (73).

Ethyl 2-Diazo-3-oxo-6-[(3-phenylprop-2-enyl)thio]hexanoate (**7f**).
Treatment of a solution of (**2a**) (355 mg, 1.64 mmol) in DMF (6 ml) with triethylamine (0.25 ml, 1.80 mmol) and cinnamyl bromide (356 mg, 1.80 mmol) gave the title compound (**7f**) (337 mg, 62%) as a low melting solid; (Found: C, 61.5; H, 6.4; N, 8.2; S, 9.9. $C_{17}H_{20}N_2O_3S$ requires C, 61.4; H, 6.1; N, 8.4; S, 9.7%); $\nu_{max.}$ (film) 2135, 1714, 1654, 1374, 1303, and 1221 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.32 (3 H, t, J 7.1 Hz, CH_2CH_3), 1.91 (2 H, quin, J 6.9 Hz , $CH_2CH_2CH_2$), 2.55 (2 H, t, J 6.9 Hz, CH_2CH_2S), 2.95 (2 H, t, J 7.3 Hz, CH_2CO), 3.28 (2 H, d, J 7.9 Hz, $CHCH_2S$), 4.26 (2 H, q, J 7.1 Hz, CO_2CH_2), 6.15 (1 H, dt, J 15.2, 7.2 Hz, $CHCH_2S$), 6.42 (1 H, d, J 15.2 Hz, PhCH), and 7.17-7.40 (5 H, m, ArH); m/z (130°C) 304 (M$^+$, 11%), 258 (3), 225 (3), 202 (4), 117 (100).

Ethyl 6-[(E)-But-2-enyl]thio-2-diazo-3-oxohexanoate (**7g**).
A solution of crude (**2a**) (250 mg, 1.16 mmol) in DMF (2 ml) was treated with triethylamine (0.20 ml, 1.4 mmol) and crotyl bromide (0.14 ml, 1.4 mmol), to give the title compound (**7g**) (163 mg, 52%) as the major product (isomer A) (~80%) together with two minor isomers: ethyl 6-[(Z)-but-2-enyl]thio-2-diazo-3-oxohexanoate (isomer B) (~10%) and ethyl 6-[(1-methylprop-2-enyl)thio]-2-diazo-3-oxohexanoate (isomer C) (~10%); (Found: M$^+$, 270.1046. $C_{12}H_{18}N_2O_3S$ requires M, 270.1038); $\nu_{max.}$ (film) 2135, 1717, 1655, 1374, 1302, and 1221 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.27 (3 H, d, J 6.5 Hz, Me, isomer C), 1.31 (3 H, t, J 7.0 Hz, CH_2CH_3), 1.63 (3 H, d, J 6.4 Hz, Me, isomer B), 1.67 (3 H, dd, J 6.0, 0.5 Hz, Me, isomer A), 1.88 (2 H, quin, J 7.2 Hz, $CH_2CH_2CH_2$), 2.49 (2 H, t, J 7.2 Hz, SCH_2), 2.94 (2 H, approx t, J 7.2 Hz, CH_2CO), 3.05 (2 H, approx d, J 7.0 Hz, $CHCH_2S$, isomer A), 3.15 (2 H, d, J 7.5 Hz, $CHCH_2S$, isomer B), 3.29 (1 H, quin, J 7.2 Hz, SCH(Me), isomer C), 4.27 (2 H, q, J 7.0

Hz, CO_2CH_2), 4.92-5.03 (2 H, m, CH:CH_2, isomer C) and 5.31-5.70 (2+2+1 H, m, CH:CH isomers A and B, and CH:CH_2 isomer C); m/z (80°C) 270 (M^+, 3%), 242 (12), 196 (11), 188 (22), 142 (43), 109 (49), and 55 (100).

Ethyl 6-Acetylthio-2-diazo-3-oxohexanoate (**7h**).
Acetic anhydride (65 µl, 0.68 mmol) was added to a solution of crude (**2a**) (118 mg, 0.546 mmol) in pyridine (0.55 ml, 6 mmol) and the mixture stirred for 5 h. Aqueous work-up, washing the ether phase with copper(II) sulphate solution, and chromatographic purification of the residue gave the title compound (**7h**) (70.0 mg, 50%) as a yellow oil, (Found: C, 46.8; H, 5.5; N, 10.6; S, 12.9. $C_{10}H_{14}N_2O_4S$ requires C, 46.5; H, 5.5; N, 10.9; S, 12.4%); $\nu_{max.}$ (film) 2136, 1718, 1694, 1656, 1375, and 1132 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.29 (3 H, t, J 7.0 Hz, CH_2CH_3), 1.89 (2 H, quin, J 7.1 Hz), 2.29 (3 H, s, COMe), 2.89 (4 H, t, J 7.1 Hz, CH_2CO and CH_2S), and 4.26 (2 H, q, J 7.0 Hz, CH_2CH_3); m/z (80°C) 258 (M^+, 3%), 226 (2), 215 (2), 188 (35), 156 (29), 142 (38), and 43 (100).

Ethyl 2-Diazo-6-[(methoxycarbonyl)acetyl]thio-3-oxohexanoate (**7i**).
Treatment of a solution of crude (**2a**) (445 mg, 2.06 mmol) in DMF (5 ml) with triethylamine (0.32 ml, 2.27 mmol) and methyl malonylchloride (281 mg, 2.06 mmol) resulted in an exothermic reaction. After 18 h, work-up and purification gave the title compound (**7i**) (305 mg, 47%) as a viscous oil; (Found: C, 45.7; H, 5.3; N, 8.8; S, 10.4. $C_{12}H_{16}N_2O_6S$ requires C, 45.6; H, 5.1; N, 8.9; S, 10.1%); $\nu_{max.}$ (film) 2138, 1748, 1717, 1691, 1654, 1376, and 1304 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.30 (3 H, t, J 7.2 Hz, CH_2CH_3), 1.92 (2 H, quin, J 7.2 Hz), 2.90 (2 H, t, J 7.1 Hz, CH_2S), 2.95 (2 H, t, J 7.1 Hz, CH_2CH_2CO), 3.28 (2 H, s, CH_2CO_2Me), 3.70 (3 H, s, CO_2CH_3), and 4.26 (2 H, q, J 7.2 Hz, CO_2CH_2); m/z (100°C) 316 (M^+, 1%), 285 (1), 274 (1), 256 (1), 242 (1), 228 (1), 215 (2), 188 (13), 142 (54), 101 (100), and 59 (61).

Ethyl 7-Benzylthio-2-diazo-3-oxoheptanoate (**7j**).
To a solution of (**2b**) (155 mg, 0.673 mmol) in DMF (2 ml) triethylamine (0.14 ml, 1.00 mmol), and benzyl bromide (84 µl, 0.71 mmol) were added. After 12 h, work-up and chromatography on neutral alumina gave the title compound (**7j**) (66 mg, 31%), as a yellow oil; (Found: C, 60.0; H, 6.5; N, 8.7. $C_{16}H_{20}N_2O_3S$ requires C, 60.0; H, 6.3; N, 8.8%); $\nu_{max.}$ (film) 2135, 1717, 1656, 1372, 1304, and 1218 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.33 (3 H, t, J 7.1 Hz, CH_2CH_3), 1.53-1.82 (4 H, m), 2.42 (2 H, t, J 7.1 Hz, CH_2S), 2.82 (2 H, t, J 7.1 Hz, CH_2CO), 3.70 (2 H, s, CH_2Ph), 4.29 (2 H, q, J 7.1 Hz,

CO_2CH_2), and 7.15-7.44 (5 H, m, ArH); m/z (120°C) 292 (M^+, 1%), 274 (1), 246 (3), 218 (1), 169 (16), 123 (48), and 91(100).

Ethyl 2-Diazo-3-oxo-7-[(3-phenylprop-2-enyl)thio]heptanoate (**7k**).
Treatment of a solution of (**2b**) (415 mg, 1.80 mmol) in DMF (4 ml) with triethylamine (0.38 ml, 2.70 mmol), and cinnamyl bromide (391 mg, 1.98 mmol) gave, after work-up and chromatography, the title compound (**7k**) (298 mg, 48%), as a yellow oil; (Found: C, 62.4; H, 7.7; N, 9.7. $C_{18}H_{22}N_2O_3S$ requires C, 62.4; H, 7.7; N, 9.7%); $\nu_{max.}$ (film) 2135, 1718, 1656, 1372, 1305, and 1218 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.33 (3 H, t, J 7.1 Hz, CH_2CH_3), 1.56-1.84 (4 H, m), 2.52 (2 H, t, J 7.1 Hz, CH_2S), 2.87 (2 H, t, J 7.1 Hz, CH_2CO), 3.31 (2 H, dd, J 7.6, 0.7 Hz, $CHCH_2S$), 4.30 (2 H, q, J 7.1 Hz, CO_2CH_2), 6.18 (1 H, dt, J 15.3, 7.5 Hz, CHCHPh), 6.44 (1 H, d, J 15.6 Hz, CHPh), and 7.20-7.43 (5 H, m, ArH); m/z (FAB; glycerol) 347 (MH^+, 4%), 318 (1), 117 (100), and 91 (15).

5-Allylthiopentanoic acid.
A solution of 5-mercaptopentanoic acid[16] (402 mg, 3.00 mmol) in dichloromethane (5 ml) at 0°C was degassed and placed under an atmosphere of nitrogen; triethylamine (0.44 ml, 3.15 mmol) and allyl bromide (0.30 ml, 3.3 mmol) were then added dropwise, in succession, and the resulting suspension was stirred for 0.75 h at 0°C and then 12 h at room temperature. Aqueous work-up and chromatographic purification gave the title compound (242 mg, 47%), the second of three components, as an oil; (Found: C, 54.9; H, 8.3; S, 18.1. $C_8H_{14}O_2S$ requires C, 55.1; H, 8.1; S, 18.4%); $\nu_{max.}$ (film) 3600-2400, 1709, 1635, 1229, and 918 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.50-1.90 (4 H, m), 2.30-2.54 (4 H, m, CH_2CO and CH_2S), 3.10 (2 H, d, J 7 Hz, $CHCH_2S$), 4.92-5.05 (1 H, m, CH:CH_2), 5.13 (1 H, d, J 2 Hz, CH:CH_2), 5.50-6.00 (1 H, m, CH_2:CH), and 11.50 (1 H, br, CO_2H); m/z (110°C) 174 (M^+, 61%), 133 (7), 114 (55), 101 (46), 73 (66), and 41 (100).

6-Allylthio-1-diazohexan-2-one (**14a**).
A solution of the above acid (173 mg, 0.993 mmol) and oxalyl chloride (0.15 ml, 1.8 mmol) in ether (5 ml) was stirred for 12 h at room temperature. All volatile material was evaporated under high vacuum to give the crude acid chloride as a viscous oil; $\nu_{max.}$ (film) 1800 cm^{-1}.
The crude acid chloride was dissolved in ether (5 ml) and an ethereal solution of diazomethane (12 ml, 4.5 mmol) added dropwise. After 18 h at room temperature the ether was slowly evaporated under a stream of nitrogen. Chromatographic

purification of the residue on Florisil gave the title compound (**14a**) (109 mg, 55%) as an unstable yellow oil; (Found: M$^+$,170.0766. $C_9H_{14}N_2OS - N_2$ requires M, 170.0765); $\nu_{max.}$ (film) 2104, 1641, and 1376 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.45-2.05 (4 H, m), 2.34 (2 H, t, J 7.0 Hz, CH_2S), 2.46 (2 H, t, J 6.5 Hz, CH_2CO), 3.11 (2 H, d, J 7 Hz, $CHCH_2S$), 4.95-5.05 (1 H, m, $CHCH_2S$), 5.14 (1 H, approx d, J 2 Hz, $CH{:}CH_2$), 5.27 (1 H, s, $CHCN_2$), and 5.55-6.00 (1 H, m, $CH{:}CH_2$); m/z (100°C) 202 (M$^+$, 1%), 170 (3), 157 (2), 142 (4), 137 (1), 129 (30), 101 (27), 67 (38), and 41 (100).

Methyl 5-(3-Phenylprop-2-enyl)pentanoate.
Cinnamyl bromide (3.31 g, 17.0 mmol) was added to a solution of methyl 5-mercaptopentanoate (2.37 g, 16.0 mmol) and triethylamine (2.46 ml, 18.0 mmol) in DMF (20 ml), and a solid was immediately. The reaction was stirred at room temperature for 24 h before aqueous work-up. The crude product was purified by chromatography and distillation to give the title compound (1.56 g, 37%) as an oil, b.p. 190-200°C at 0.3 mmHg; (Found: M$^+$, 264.1176. $C_{15}H_{20}O_2S$ requires M, 264.1184); $\nu_{max.}$ (film) 1738, 1436, 1206, 1174, and 754 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.53-1.80 (4 H, m), 2.33 (2 H, t, J 7.0 Hz, CH_2CO), 2.50 (2 H, t, J 7.0 Hz, CH_2S), 3.30 (2 H, dd, J 7.3, 1.0 Hz, $CHCH_2S$), 3.65 (3 H, s, OMe), 6.18 (1 H, dt, J 15.5, 7.3 Hz, $CHCHPh$), 6.43 (1 H, d, J 15.5, 7.3 Hz, $CHCHPh$), and 7.19-7.42 (5 H, m, ArH); m/z (150°C) 264 (M$^+$, 8%), 234 (2), 134 (14), 117 (100), and 91 (30).

5-(3-Phenylprop-2-enyl)pentanoic acid.
A solution of potassium hydroxide (2.0 g) in water (10 ml) was added to a solution of the above ester (1.00 g, 3.79 mmol) in methanol. The reaction was stirred at room temperature for 24 h. Work-up gave the title compound (0.97 g, 100%) as a pale solid, which was used in the next step without further purification. A small sample was recrystallised, m.p. 79-80°C (ether/petrol); (Found: C, 67.1; H, 7.3. $C_{14}H_{18}O_2S$ requires C, 67.2; H, 7.3%); $\nu_{max.}$ (film) 3500-2500, 1698, 1040, 1286, 1228, 969, and 750 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.50-1.83 (4 H, m), 2.38 (2 H, t, J 6.9 Hz, CH_2CO), 2.51 (2 H, t, J 6.9 Hz, CH_2S), 3.30 (2 H, dd, J 7.2, 1.0 Hz, $CHCH_2S$), 6.18 (1 H, dt, J 15.6, 7.2 Hz, $CHCHPh$), 6.42 (1 H, d, J 15.6, $CHCHPh$), 7.15-7.42 (5 H, m, ArH), and 9.70 (1 H, br, CO_2H); m/z (100°C) 250 (M$^+$, 17%), 149 (6), 134 (1), 117 (100), and 91 (8).

1-Diazo-6-(3-phenylprop-2-enyl)thiohexan-2-one (**14b**).
A solution of the above acid (0.909 g, 3.63 mmol) and oxalyl chloride (0.34 ml, 1.80 mmol) in benzene (50 ml) was stirred for 18 h at room temperature. All volatile

material was evaporated under high vacuum and the residue distilled to give 5-(3-phenylprop-2-enyl)pentanoyl chloride (0.529 g, 52%), as a viscous oil; b.p. 165°C at 2 mmHg; $\nu_{max.}$ (film) 1800 cm^{-1}.

The acid chloride (490 mg, 1.82 mmol) was dissolved in ether (10 ml) and an ethereal solution of diazomethane (20 ml, 6.0 mmol) added dropwise. After 14 h at room temperature the ether was slowly evaporated under a stream of nitrogen. Chromatographic purification of the residue on Florisil gave the title compound (**14b**) (245 mg, 49%) as an unstable yellow oil; (Found: M$^+$, 246.1080. $C_{15}H_{18}N_2OS$ requires M, 246.1078); $\nu_{max.}$ (film) 2103, 1641, 1379, 1323, 965, and 754 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.45-1.72 (4 H, m), 2.23 (2 H, approx t, J 6.0 Hz, CH_2CO), 2.40 (2 H, t, J 7.1 Hz, CH_2S), 3.20 (2 H, dd, J 7.1, 1.0 Hz, $CHCH_2S$), 5.20 (1 H, br, CHN_2), 6.19 (1 H, dt, J 15.4, 7.1 Hz, CHCHPh), 6.44 (1 H, d, J 15.4, CHCHPh), and 7.20-7.42 (5 H, m, ArH); m/z (FAB; glycerol) 275 (MH$^+$, 1%), and 117 (100).

Rhodium Carbenoid Mediated Cyclisation of Diazosulphides

Ethyl 1-Benzyl-3-oxo-3,4,5,6-tetrahydrothiabenzene-2-carboxylate (**8**).

A solution of (**7b**) (120 mg, 0.392 mmol) in benzene (5 ml) was added to a suspension of dirhodium tetraacetate (5 mg) in boiling benzene (10 ml) over 8 min and reflux was continued for a further 5 min. The solvent was evaporated to give a solid, which was purified by crystallisation to give the title compound (**8**) (26 mg, 24%) as colourless crystals, m.p. 134-135°C (benzene/hexane); (Found: C, 64.6; H, 6.5; S, 11.4. $C_{15}H_{18}O_3S$ requires C, 64.7; H, 6.5; S, 11.5%); $\nu_{max.}$ (Nujol) 1681, 1606, 1577, 1374, 1250, 1056, and 710 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.36 (3 H, t, J 7.0 Hz, CH_2CH_3), 2.10-2.40 (4 H, m, CH_2CH_2CO), 2.78-3.05 (2 H, m, CH_2S), 3.97 (1 H, d, J 13.1 Hz, CH_2Ph), 4.19-4.39 (2 H, m, CO_2CH_2), 4.60 (1 H, d, J 13.1 Hz, CH_2Ph), and 7.30-7.48 (5 H, m, ArH); m/z (150°C) 262 (M$^+$, 8%), 232 (2), 188 (3), 142 (15), 115 (6), and 91 (100).

Ethyl 2-Benzyl-3-oxothiane-2-carboxylate (**9**).

A suspension of (**8**) (11.4 mg, 41 μmol) in xylene (4 ml) was quickly brought to reflux and maintained at reflux for 2.5 h. The solvent was evaporated and the residue purified by chromatography to give the title compound (**9**) (6.3 mg, 55%) as a low melting solid, m.p. 45-48°C; (Found: M$^+$, 278.0974. $C_{15}H_{18}O_3S$ requires M, 278.0977); $\nu_{max.}$ (melt) 1746, 1712, 1670, 1242, and 1181 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.19 (3 H, t, J 7.0 Hz, CH_2CH_3), 2.26-2.66 (6 H, m, $(CH_2)_3$), 2.97 (1 H, d, J 14.3 Hz, CH_2Ph), 3.52 (1 H, d, J 14.3 Hz, CH_2Ph), 4.13 (2 H, dq, J 7.0, 0.7 Hz, CO_2CH_2), and 7.05-7.38 (5 H, m, ArH); m/z (120°C) 278 (M$^+$, 28%), 232 (2), 218 (2), 205 (10), 187

(6), 177 (3), 172 (6), 159 (7), 116 (14), and 91 (73).

Ethyl 3-Oxothiepane-2-carboxylate (**3b**) [from (**7j**)].
A solution of (**7j**) (51 mg, 0.16 mmol) in benzene (4 ml) was added over 5 min to a suspension of dirhodium tetraacetate (2 mg) in benzene (10 ml) at reflux. After 5 min at reflux, extra catalyst (2 mg) was added. After a further 15 min, the reaction mixture was cooled, evaporated, and the residue chromatographed to give the title compound (**3b**) (2.1 mg, 7%), identical to the previously prepared material.

Ethyl 2-Allyl-3-oxothiane-2-carboxylate (**11a**).
A solution of (**7d**) (400 mg, 1.56 mmol) in benzene (10 ml) was added to a suspension of dirhodium tetraacetate (9 mg) in benzene (30 ml) at reflux over 10 min. After 5 min at reflux the green mixture was cooled, filtered, evaporated and the residue subjected to chromatography to give the title compound (**11a**) (210 mg, 59%) as an oil; (Found: C, 57.9; H, 7.3; S, 14.1. $C_{11}H_{16}O_3S$ requires C, 57.9; H, 7.1; S, 14.0%); $\nu_{max.}$ (film) 1746, 1714, 1641, 1220, and 1189 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.29 (3 H, t, J 7.2 Hz, CH_2CH_3), 2.24-2.62 (6 H, m), 2.82 (1 H, ddt, J 14.5, 7.2, 1.2 Hz, $CH_2CH{:}CH_2$), 3.03 (1 H, ddd, J 13.2, 11.5, 3.4 Hz, CH_2CO), 4.26 (2 H, dq, J 7.2, 1.0 Hz, CH_2CH_3), 5.05-5.15 (2 H, m, $CH_2{:}CH$), and 5.74 (1 H, dddd, J 17.3, 9.5, 7.4, 6.6 Hz, $CH_2{:}CH$); m/z (140°C) 228 (M^+, 99%), 200 (11), 187 (32), 155 (63), 127 (50), 113 (22), 85 (100), and 41 (61).

Ethyl 2-(1,1-Dimethylprop-2-enyl)-3-oxothiane-2-carboxylate (**11b**).
A solution of (**7e**) (148 mg, 0.521 mmol) in benzene (6 ml) was added to a suspension of dirhodium tetraacetate (4.3 mg) in benzene (20 ml) at reflux over 5 min. Reflux was continued for 25 min. Evaporation of solvent and chromatography of the residue gave the title compound (**11b**) (88 mg, 66%) as a clear oil, b.p. 130°C at 0.5 mmHg; (Found: M^+, 256.1132. $C_{17}H_{20}O_3S$ requires M, 256.1133); $\nu_{max.}$ (film) 1741, 1713, 1635, and 1219 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.24 (3 H, s, Me), 1.27 (3 H, s, Me), 1.29 (3 H, q, J 7.0 Hz, CH_2CH_3), 2.23-2.37 (2 H, m, CH_2CH_2S), 2.38-2.53 (2 H, m, CH_2S), 2.58 (1 H, ddd, J 14.0, 3.7, 1.1 Hz, CH_2CO), 2.77-2.90 (1 H, m, CH_2CO), 4.27 (2 H, dq, J 7.5, 0.6 Hz, CO_2CH_2), 4.98 (1 H, dd, J 5.9, 1.1 Hz, $CH{:}CH_2$), 5.05 (1 H, s, $CH{:}CH_2$), and 6.26 (1 H, approx dd, J 15.6, 10.8 Hz, $CH{:}CH_2$); m/z (100°C) 256 (M^+,19%), 188 (60), 183 (4), 142 (100), 69 (30), and 41 (26).

Ethyl 3-Oxo-2-(1-phenylprop-2-enyl)thiane-2-carboxylate (**11c**).
A solution of (**7f**) (121 mg, 0.364 mmol) in benzene (6 ml) was added to a suspension of dirhodium tetraacetate (1.9 mg) in benzene (10 ml) at reflux over 7 min. Reflux of the mauve solution was continued for 20 min. Evaporation of solvent and chromatography of the residue gave the title compound (**11c**) (86 mg, 78%), a low melting solid, as a mixture of two diastereomers (7:3), m.p. 58-63°C, b.p. 130-140°C at 0.0005 mmHg; (Found: C, 66.8; H, 6.6; S, 10.5. $C_{17}H_{20}O_3S$ requires C, 67.1; H, 6.6; S, 10.5%); $\nu_{max.}$ (film) 1742, 1713, 1635, 1453, 1219, 1189, 1028, and 703 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.00 (3 H, t, J 6.9 Hz, CH_2CH_3, minor diastereomer), 1.21 (3 H, t, J 6.9 Hz, CH_2CH_3, major diastereomer), 2.20-2.45 (2 H, m), 2.45-2.64 (3 H, m), 2.87 (1 H, ddd, J 14.6, 10.2, 4.0 Hz, HCHS, major diastereomer), 2.97-3.13 (1 H, m, HCHS, minor diastereomer), 3.80-4.01 (2 H, m, CO_2CH_2, minor diastereomer), 4.18 (3 H, dq, J 6.6, 2.2 Hz, CO_2CH_2 and CHPh, major diastereomer), 4.49 (1 H, d, J 6.3 Hz, CHPh, minor diastereomer), 4.87-5.20 (2 H, m, $CH{:}CH_2$), 6.10-6.40 (1 H, m, $CH{:}CH_2$), and 7.15-7.40 (5 H, m, ArH); m/z (160°C) 304 (M^+, 6%), 286 (2), 258 (3), 229 (1), 213 (1), 188 (2), 161 (1), 142 (4), 129 (6), and 117 (100).

Ethyl 2-(1-Methylprop-2-enyl)-3-oxothiane-2-carboxylate (**11d**).
A solution of (**7g**) (83 mg, 0.307 mmol) in benzene (5 ml) was added to a suspension of dirhodium tetraacetate (2.3 mg) in benzene (10 ml) at reflux over 9 min. After 5 min at reflux the suspension was cooled, filtered, evaporated, and the residue subjected to chromatography to give the title compound (**11d**) (52.6 mg, 71%) (isomer A) an oil, as a mixture of two diastereomers (2:1), together with ethyl 2-(but-2-enyl)-3-oxothiane-2-carboxylate (isomer B) (~14% of total product), b.p. 175°C at 1.8 mmHg; (Found: C, 59.4; H, 7.6. $C_{12}H_{18}O_3S$ requires C, 59.5; H, 7.5%); $\nu_{max.}$ (film) 1743, 1713, 1639, 1447, 1221, and 1192 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.05 (3 H, d, J 6.9 Hz, Me, minor diastereomer), 1.12 (3 H, d , J 6.9 Hz, Me, major diastereomer), 1.26 (3 H, t, J 7.1 Hz, CH_2CH_3, major diastereomer A, and isomer B), 1.30 (3 H, t, J 7.1 Hz, CH_2CH_3, minor diastereomer), 1.61 (3 H, dd, J 6.9, 0.5 Hz, Me, isomer B), 2.17-2.65 (~5 H, m), 2.68-3.15 (~2 H, m), 4.20 (2 H, q, J 6.7 Hz, $COCH_2$, major diastereomer), 4.26 (2 H, q, J 6.7 Hz, $COCH_2$, isomer B), 4.28 (2 H, dq, J 6.7, 0.7 Hz, $COCH_2$, minor diastereomer), 4.94-5.10 (2 H, m, $CH{:}CH_2$, isomer A), 5.25-5.47 (2 H, m, $CH{:}CH$, isomer B), and 5.72-5.92 (1 H, m, $CH{:}CH_2$, isomer A); m/z (130°C) 242 (M^+, 38%), 196 (3), 188 (64), 142 (100), and 99 (15).

Ethyl 3-Oxo-2-(1-phenylprop-2-enyl)thiepane-2-carboxylate (**13**).
A solution of (**7k**) (100 mg, 0.289 mmol) in benzene (5 ml) was added over 5 min to a suspension of dirhodium tetraacetate (2 mg) in benzene (15 ml) at reflux. After 2

min at reflux, extra catalyst (2 mg) was added and reflux continued for 12 min. The reaction mixture was allowed to cool, evaporated and the residue purified by chromatography to give the title compound (**13**) (27 mg, 26%), an oil, as a mixture of diastereomers (3:2); (Found: C, 67.7; H, 7.2. $C_{18}H_{22}O_3S$ requires C, 67.9; H, 7.0%); $\nu_{max.}$ (film) 1735, 1713, 1636, 1453, 1224, 1189, 1150, 1103, and 703 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.12 (3 H, J 7.1 Hz, CH_2CH_3, minor diastereomer), 1.21 (3 H, J 7.0 Hz, CH_2CH_3, major diastereomer), 1.53-1.90 (4 H, m), 2.02-2.20 (1 H, m), 2.52-2.91 (3 H, m), 3.94-4.09 (2 H, m, CO_2CH_2, minor diastereomer), 4.16 (2 H, dq, J 6.9, 1.0 Hz, CO_2CH_2, major diastereomer), 4.28 (1 H, t, J 8.6 Hz, CHPh), 5.08-5.24 (2 H, m, CH_2:CH), 6.36-6.50 (1 H, m, CHCHPh), 7.16-7.32 (3 H, m, ArH), and 7.41-7.54 (2 H, m, ArH); m/z (120°C) 318 (M^+, 4%), 300 (11), 272 (3), 243 (4), 214 (3), 156 (3), 129 (11), and 117 (100).

2-Allylthiepan-2-one (**15a**).

A solution of (**14a**) (82 mg, 0.414 mmol) in benzene (8 ml) was added dropwise to a suspension of dirhodium tetraacetate (3 mg) in benzene (10 ml) at reflux. After 1 h, the pink solution was cooled, evaporated, and the residue subject to chromatography to give the title compound (**15a**) (30 mg, 42%) as an oil, b.p. 100°C at 0.8 mmHg (Found: M^+, 170.0768. $C_9H_{14}OS$ requires M, 170.0765); $\nu_{max.}$ (film) 1699, 1641, and 918 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.60-1.95 (3 H, m), 2.00-2.17 (1 H, m), 2.34 (1 H, ddt, J 14.7, 7.4, 1.3 Hz), 2.58-2.73 (4 H, m), 2.80 (1 H, ddd, J 14.2, 10.6, 3.2 Hz, $SCHCH_2$), 3.57 (1 H, dd, J 7.9, 6.6 Hz, $SCHCH_2$), 5.00-5.16 (2 H, m, $CH:CH_2$), and 5.82 (1 H, ddt, J 17.4, 10.2, 7.0 Hz, $CH:CH_2$); m/z (140°C) 170 (M^+, 22%), 129 (12), 105 (31), 101 (30), and 41 (100).

2-(1-Phenylprop-2-enyl)thiepan-3-one (**15b**).

A solution of (**14b**) (153 mg, 0.558 mmol) in benzene (7.5 ml) was added over 5.5 min to a suspension of dirhodium tetraacetate (4 mg) in benzene (20 ml) at reflux. After 3 min at reflux, the reaction mixture was cooled, evaporated and the residue purified by chromatography on silica gel to give the title compound (**15b**) (87 mg, 64%), a low melting solid, as a mixture of two diastereomers, m.p. 35-38°C, b.p. 145-155°C at 0.25 mmHg; (Found: C, 73.1; H, 7.4. $C_{15}H_{18}OS$ requires C, 73.1; H, 7.4%); $\nu_{max.}$ (film) 1699, 1637, 1453, 1200, 922, and 701 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.54-1.80 (2 H, m), 1.80-2.15 (2 H, m), 2.30-2.43 (1 H, m, CH_2CO), 2.49 (1 H, ddd, J 12.4, 6.6, 2.3 Hz, CH_2CO), 2.63 (1 H, approx dd, J 14.9, 7.4 Hz, CH_2S), 2.72-2.85 (2 H, m, CH_2S, minor diastereomer), 2.92 (1 H, approx ddd, J 13.2, 10.7, 2.7 Hz, CH_2S, major diastereomer), 3.78 (1 H, approx t, J 8.7 Hz, CHPh, major diastereomer), 3.86

(1 H, t, J 8.3 Hz, CHPh, minor diastereomer), 3.98 (1 H, d, J 8.7 Hz, CHS, minor diastereomer), 4.01 (1 H, d, J 9.9 Hz, CHS, major diastereomer), 4.98-5.20 (2 H, m, CH:CH_2), 5.92-6.18 (1 H, m, CH:CH_2), and 7.17-7.32 (5 H, m, ArH); m/z (120°C) 246 (M^+, 16%), 157 (3), 129 (12), and 117 (100); together with a second compound formed by addition of the carbenoid to the benzene solvent: 1-[5-(3-phenylprop-2-enyl)thiolpentanoylcyclohepta-2,4,6-triene (21 mg, 12%), an oil; (Found: M^+, 324.1543. $C_{21}H_{24}OS$ requires M, 324.1548); $\nu_{max.}$ (film) 1717, 1600, 1450, 1288, 965, 751, and 703 cm^{-1}; δ_H (270 MHz; $CDCl_3$) 1.45-1.78 (4 H, m), 2.37 (1 H, t, J 5.6 Hz, CHCO), 2.48 (2 H, t, J 6.8 Hz, CH_2CO), 2.55 (2 H, t, J 6.8 Hz, CH_2S), 3.31 (2 H, d, J 7.3 Hz, SCH_2CH), 5.02 (2 H, dd, J 7.6, 5.6 Hz, CHCHCO), 6.17 (1 H, dt, J 15.6, 7.5 Hz, CHCHPh), 6.26-6.31 (2 H, m, CHCHCHCO), 6.43 (1 H, d, J 15.8 Hz, CHPh), 6.57 (2 H, dd, J 3.1, 2.8 Hz, CH:CHCH), and 7.08-7.25 (5 H, m, ArH); m/z (120°C) 324 (M^+, 1%), 246 (9), 203 (10), 129 (30), 117 (100), and 91 (54).

Ethyl 1-Ethyl-3-oxo-3,4,5,6-tetrahydrothiabenzene-2-carboxylate (**16**).
A solution of (**7a**) (20.0 mg, 0.082 mmol) in benzene (8 ml) was rapidly heated to reflux and dirhodium tetraacetate (1.3 mg) added. Reflux was continued for 5 min. After cooling, the mixture was filtered through cotton wool, evaporated, and the residue recrystallised to give the title compound (**16**) (11 mg, 62%), m.p. 116-118°C; (Found: M^+, 216.0815. $C_{10}H_{16}O_3S$ requires M, 216.0820); $\nu_{max.}$ (Nujol) 1674, 1543, 1370, 1204, and 1051 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.32 (3 H, t, J 7.0 Hz, CH_2CH_3), 1.36 (3 H, t, J 7.4 Hz, CH_2CH_3), 2.13-2.48 (4 H, m, CH_2CH_2CO), 2.90-3.31 (4 H, m, CH_2SCH_2), and 4.16-4.32 (2 H, m, CO_2CH_2); m/z (140°C) 216 (M^+, 100%), 188 (71), 171 (24), 159 (26 (68), 113 (59), and 85 (54).

Ethyl 3-Oxothiane-2-carboxylate (**3a**) [from (**7a**)].
A solution of (**7a**) (52.5 mg, 0.215 mmol) in xylene (5 ml) was added to a suspension of dirhodium tetraacetate (1.5 mg) in xylene (5 ml) at reflux over 8 min. After 20 min at reflux, evaporation of solvent and chromatography of the residue gave the title compound (**3a**) (34 mg, 84%), identical to the previously prepared sample.

Ethyl 3-Oxothiane-2-carboxylate (**3a**) [from (**7i**)].
A solution of (**7i**) (210 mg, 0.665 mmol) in benzene (8 ml) was added to a suspension of dirhodium tetraacetate (4.9 mg) in benzene (22 ml) at reflux over 5 min. After 5 min at reflux, the reaction mixture was cooled, the solvent evaporated, and the residue was purified by chromatography to give the title compound (**3a**) (16 mg, 13%), identical to the previously prepared sample.

Ethyl 2-Acetyl-3-oxothiane-2-carboxylate (**17**).
A solution of (**7h**) (44.9 mg, 0.174 mmol) in benzene (15 ml) was rapidly heated to reflux and dirhodium tetraacetate (1.5 mg) added. Reflux was continued for 10 min. After cooling, the mixture was filtered, evaporated, and the residue subjected to chromatography to give the title compound (**17**) (16 mg, 40%) as an oil; (Found: M^+, 188.0505. $C_{10}H_{14}O_4S$ requires M, 188.0507); $\nu_{max.}$ (film) 1746, 1734, 1712, 1241, and 1181 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.20 (3 H, t, J 7.1 Hz, CH_2CH_3), 2.26 (3 H, s, COMe), 2.18-2.45 (2 H, m, CH_2CH_2S), 2.48-2.80 (4 H, m), and 4.23 (2 H, q, J 7.1 Hz, CO_2CH_2); m/z (100°C) 230 (M^+, 1%), 202 (2), 188 (14), 160 (3), 142 (27), 116 (5), 103 (13), and 83 (100).

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REFERENCES AND NOTES

1. Part 4, M. J. Davies, J. C. Heslin, and C. J. Moody, *J. Chem. Soc., Perkin Trans. 1,* 1989, 2473.
2. W. Ando, *Acc. Chem. Res.,* 1977, **10**, 179.
3. G. Maas, *Top. Curr. Chem.,* 1987, **137**, 75.
4. M. P. Doyle, *Chem. Rev.,* 1986, **86**, 919
5. M. Hori, T. Kataoka, H. Shimizu, M. Kataoka, A. Tomoto, and M. Kishida, *Tetrahedron Lett.,* 1983, **24**, 3733 and references therein.
6. For example, see:
   T. Kametani, H. Yukawa, and T. Honda, *J.Chem. Soc., Perkin Trans. 1,* 1988, 833.
   T. Kametani, K. Kawamura, and T. Honda, *J. Am. Chem. Soc.,* 1987, **109**, 3010.
   K. Prassad, G. Schulz, C. P. Mak, H. Hamberger, and P. Stutz, *Heterocycles,* 1981, **16**, 1305.
7. H. M. L. Davies and L. Van T. Crisco, *Tetrahedron Lett.,* 1987, **28**, 371.
8. Preliminary communications:
   (a) C. J. Moody and R. J. Taylor, *Tetrahedron Lett.,* 1987, **28**, 5351.
   (b) *ibid.*,1988, **29**, 6005.
9. C. J. Moody and R. J. Taylor, *J. Chem. Soc., Perkin Trans.1*,1989, 721.
10. M. J. Davies, C. J. Moody, and R. J. Taylor, *Synlett,* 1990, 93.

11. J. B. Hendrickson and W. A. Wolf, *J. Org. Chem.*, 1968, **33**, 3610.
12. M. Regitz, A. Liedhegener, U. Eckstein, M. Martin, and W. Anschutz, *Annalen*, 1971, **748**, 207.
13. M. P. Moyer, P. L. Feldman, and H. Rapoport, *J. Org. Chem.*, 1985, **50**, 5223.
14. H. Fliri, C.-P. Mak, K. Prassad, G. Schulz, and P. Stutz, *Heterocycles*, 1983, **20**, 205.
15. For the use of this rearrangement in the synthesis of large ring sulphides, see: E. Vedejs, *Acc. Chem. Res.*, 1984, **17**, 358.
16. C. G. Overburger and J. K. Weise, *J. Am. Chem. Soc.*, 1968, **90**, 3533.
17 J. C. Heslin and C. J. Moody, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1417.