α-Thio-substituted Ketones as Precursors of Olefins *via* Oxathiolanes: Benzyl as Protecting Group

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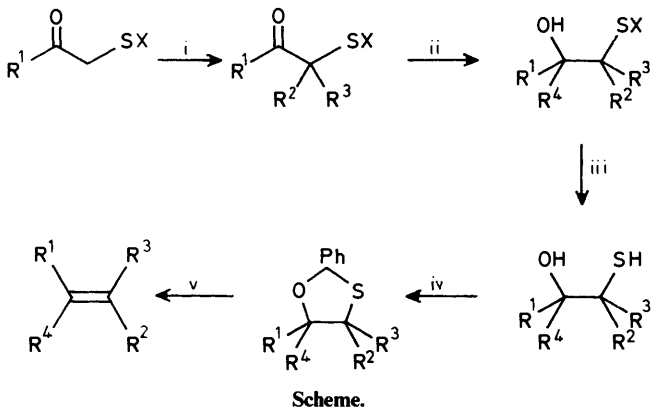
The feasibility of a regiospecific synthesis of tetrasubstituted olefins starting from protected α-thiol substituted ketones has been demonstrated by three examples. The approach (see Scheme) involves: *S*-activated alkylation (i), carbonyl addition of an organometallic reagent (ii), deprotection (iii), formation of a 2-phenyloxathiolane (iv), and base-promoted cycloelimination (v). An unsatisfactory feature is the lack of stereochemical control in step (ii).

An attempt to telescope steps (iii) and (iv) by sequential Pummerer reaction–cyclisation at the β-benzylthio alcohol stage was unsuccessful.

In the previous paper,[1] we put forward a possible sequential synthesis of tri- and particularly tetra-substituted olefins *via* 2-phenyl-1,3-oxathiolanes (Scheme) and described some of the

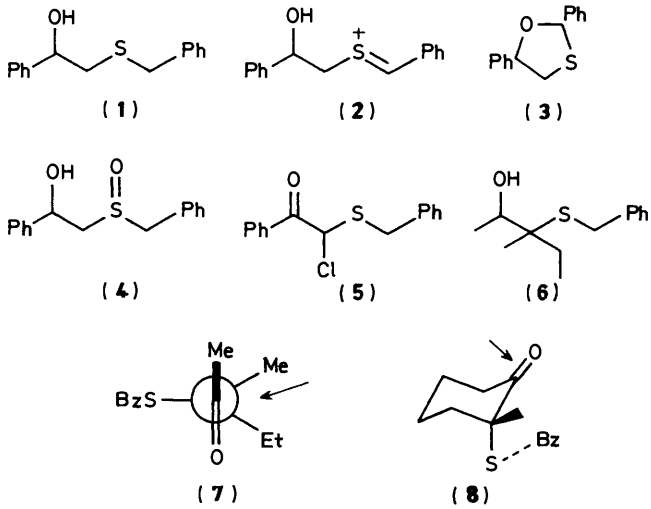


Scheme.

difficulties encountered in attempts to use α-methoxybenzyl as a protecting group [X = CH(OMe)Ph]. Since these difficulties stemmed from the lability of the hemithioacetal towards strong bases and organometallic reagents, we decided to switch to the benzyl group [X = CH_2Ph] since it has been used successfully before for protection of SH.[2]

One variant which was explored in a preliminary way before the approach in the Scheme was addressed was that of converting the *S*-benzylmercapto alcohol into the oxathiolane by oxidation–cyclisation. Thus experiments were carried out on the simple model 2-benzylthio-1-phenylethanol (**1**) under Pummerer reaction conditions[3] in the hope that the intermediate (**2**) might be formed and cyclised directly to 2,5-diphenyl-1,3-oxathiolane (**3**). In fact, treatment with *N*-chlorosuccinimide[4] (NCS) gave the sulphoxide (**4**) as major product and the known[5] oxathiolane (**3**) could not be detected. The sulphoxide (**4**) was obtained as a mixture of diastereoisomers, the ratio being dependent on reaction conditions. Hydroxy participation in the oxidation of sulphides to sulphoxides has been invoked previously,[6] albeit *via* five- or six-membered ring intermediates, and it is assumed that the four-membered ring equivalent is involved here. Attempts to convert the sulphoxide (**4**) into the oxathiolane (**3**) by Pummerer reaction using acetic anhydride[7] or trifluoroacetic anhydride[8] were unavailing.

The above-mentioned hydroxy participation is obviously excluded in the oxidation of 2-benzylthioacetophenone (**9**) and it was expected that halogenation α to sulphur would occur with



NCS. There is, however, ambiguity as to the site of reaction. In fact treatment with NCS gave the α-chloro ketone (**5**) as shown by ^1H n.m.r. comparison with the product derived from the α,α-dideuterio ketone. Clearly the greater acidity of the proton α to carbonyl directs functionalisation to this position. The non-enolisable dialkylated ketone (**14**) was recovered largely unchanged after treatment with NCS in toluene.

In the present paper, we describe the preparation of four representative α-benzylthio ketones [(**9**)—(**12**) (Table 1)] by treatment of the appropriate α-halogeno ketone with toluene-α-thiol–Et_3N in ether.

Monoalkylation of the relevant α-benzylthio ketone to give ketones (**13**), (**14**), and (**16**)—(**18**), Table 1, was achieved using sodium hydride (slight excess) in tetrahydrofuran (THF) followed by methyl or ethyl iodide as appropriate. For ketone (**10**) monomethylation did not occur cleanly under these conditions, and we used 1 mol equiv. of sodium t-pentoxide in benzene (Conia's base)[9] for the preparation of the methylated ketone (**15**).

For the next stage of the sequence (step ii, Scheme), we confined our attention to additions of methyl and ethyl Grignard and lithium reagents. The results are summarised in Table 2. In general yields were satisfactory. For the acyclic ketones (**16**) and (**17**), the diastereoselectivity of the addition, based on the stereochemistry of the olefins eventually produced, was low (of the order of 2:1). This was disappointing but was probably only to be expected for a reaction where the crucial

Table 1. Olefins from α-benzylthio ketones *via* 2-phenyloxathiolanes

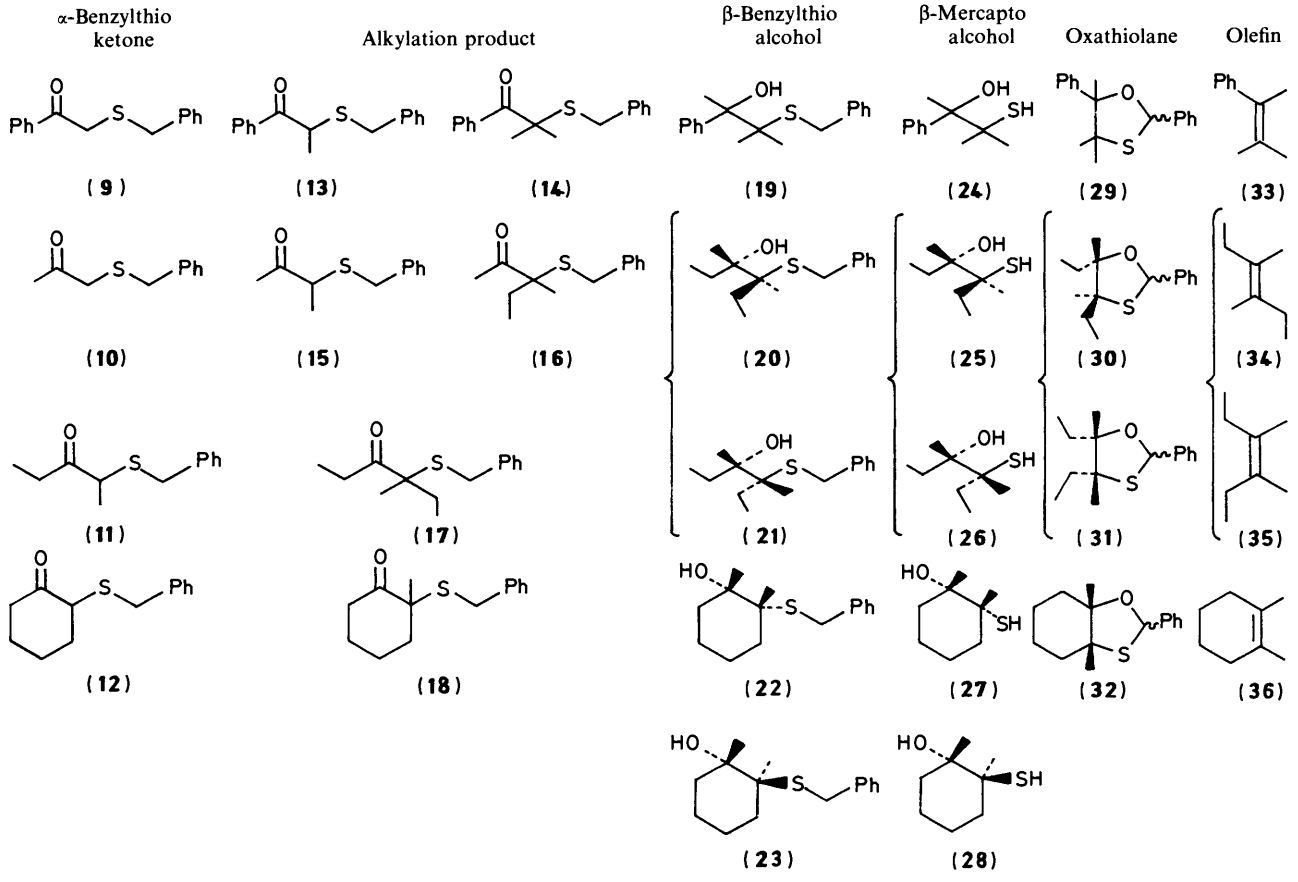


Table 2. Reaction of α-benzylthio ketones with Grignard or organolithium reagents

Entry	Ketone	Reagnets/Conditions	Yield (%)	Product(s) (%)
1	(**14**)	MeLi–LiBr–Et_2O/20 °C	80[a]	(**19**)
2	(**16**)	EtLi–C_6H_6–Et_2O/2—20 °C	89[b]	(**20**), 38; (**21**), 62
3	(**16**)	EtMgBr–Et_2O/35 °C	99[b]	(**16**), 20; (**20**), 19; (**21**), 36; (**6**) 20
4	(**17**)	MeMgI–THF/0 °C–reflux	52[a]	(**17**), 30; (**20**), 35; (**21**), 35
5	(**17**)	MeMgI–$MgBr_2$–EtO/reflux	71[b]	(**20**), 60; (**21**), 40
6	(**17**)	MeLi–LiBr–Et_2O/−78 °C ⟶ 20 °C	66[c]	(**20**), 68; (**21**), 32
7	(**17**)	$LiMe_2Cu$–MeLi–Et_2O/−65—0 °C	95[b]	(**17**), 50; (**20**), 33; (**21**), 17
8	(**18**)	MeMgI–Et_2O/reflux	94[b]	(**22**), 75; (**23**), 25
9	(**18**)	MeLi–LiBr–Et_2O/−78 °C–reflux	97[b]	(**22**) > 97

[a] After chromatography. [b] Crude yield. [c] After distillation.

step involved attack *syn-* or *anti-* to a methyl *versus* an ethyl group. The major products from ketones (**16**) and (**17**) are those which would be expected from the Felkin–Anh model;[10] *e.g.* diagram (**7**) depicts the formation of product (**21**) by attack of ethyl-lithium on ketone (**16**). Apparently α-benzylthio ketones unlike α-benzyloxy ketones[11] do not benefit from chelation control in Grignard reactions. We also tried reaction with methyltitanium tri-isopropoxide,[12] since Reetz[13] has found improved 'non-chelation control' with this reagent in a number of instances. However ketones (**17**) and (**18**) were recovered largely unchanged, being apparently too sterically hindered to react at a practicable rate.

For the cyclic ketone (**18**) fairly high diastereoselectivity was found, particularly on reaction with methyl-lithium (Table 2, entry 9). Here the stereochemical assignment of the products was based partly on an alternative synthesis of the β-benzylthio alcohol (**23**) *via trans*-opening[14,15] of 1,2-dimethylcyclohexane oxide with the lithium salt of toluene-α-thiol. It is not really clear why there should be such a high proclivity for attack *trans* to the thiobenzyl group in ketone (**18**) particularly since 2-cyano-2-methylcyclohexanone undergoes predominant attack *cis* to cyano with methylmagnesium iodide or methyl-lithium.[15] Coupling constants observed for 2-H in 2-benzylthiocyclohexanone (**12**) and 2-ethylthiocyclohexanone[16] are 5.5, 5.5, and 1, and 4.5, 4.5, and 1 Hz, respectively. We consider these values to indicate that the α-thio substituent is predominantly axially orientated and if this is also true for ketone (**18**), the possibility exists for weak complexation of the phenyl group on one face of

the carbonyl group, the *Si* face for the enantiomer shown in compound (**8**), which could favour axial attack from the opposite side as shown for compound (**8**).

The β-mercapto alcohols (**24**)—(**28**) were prepared from the β-benzylthio alcohols by reductive removal of the *S*-benzyl group using sodium in ammonia (step iii, Scheme). Since β-mercepto alcohols are not very stable, they were not purified with the exception of compound (**27**) which is a solid, but were taken directly through to step (iv). The diastereoisomers (**25**) and (**26**) were obtained as a mixture and the ^{1}H n.m.r. spectra indicated they were formed from the starting β-benzylthio alcohols (**20**) and (**21**) without loss of stereochemical integrity.

2-Phenyl-1,3-oxathiolanes (**29**)—(**32**) were prepared from the corresponding mercapto alcohols by condensation with benzaldehyde in the presence of the minimum amount of toluene-*p*-sulphonic acid (step iv, Scheme). Mercapto alcohol (**28**) was unstable under the reaction conditions and none of the corresponding oxathiolane, which would be appreciably strained, was detected.

The substituted oxathiolanes (**29**) and (**32**) were converted into the corresponding olefins 2-methyl-3-phenylbut-2-ene (**33**) and 1,2-dimethylcyclohexene (**36**) in 75 and 92% yields, respectively, on treatment with lithium di-isopropylamide (LDA) in ether at 20 °C (step v, Scheme). Because of the small scale of the experiments, yields were determined by g.l.c. using an internal standard. For the oxathiolanes (**30**) and (**31**), two different diastereoisomeric mixtures were subjected to the base-induced cycloelimination conditions. Because of complications caused by the extra chiral centre, C-2 in the oxathiolanes (**30**) and (**31**), gross diastereoisomer ratios, *i.e.* relative configurations at C-4 and C-5, were considered to be the same as in the precursor β-benzylthio alcohols (**20**) and (**21**). A mixture of compounds (**30**) and (**31**) rich in (**30**) gave 3,4-dimethylhex-3-ene rich in the *E*-isomer (**34**) and a mixture rich in the oxathiolane (**31**) gave predominantly the *Z*-olefin (**35**). There was satisfactory correspondence between the diastereoisomer ratio (**20**):(**21**) and that of the derived olefins as expected for a concerted *syn*-elimination (step v, Scheme). Stereochemical identification of *E*-and *Z*-3,4-dimethylhex-3-enes was based on the work of Reichel[17] together with the correction made by White and Greene.[18].

The potential of this stepwise route to tetrasubstituted olefins has thus been demonstrated notwithstanding the limited nature of these investigations. If a general way round the problem of controlling stereochemistry at step (ii) (Scheme) can be found, the stereospecificity of the cycloelimination step could be usefully exploited.

Experimental

^{1}H N.m.r. spectra were recorded on Perkin-Elmer R24 (60 MHz) or Bruker WH300 (300 MHz) instruments using Me_4Si as internal standard. ^{13}C N.m.r. spectra: $CDCl_3$ solutions on Bruker WH90 (22.63 MHz) or WH300 (75.43 MHz) instruments using solvent (δ_C 77.00) as internal standard.

2-Benzylsulphinyl-1-phenylethanol.—(i) A solution of 2-benzylthio-1-phenylethanol (**1**) (0.4 g) in toluene (5 ml) was added dropwise to a stirred suspension of NCS (0.22 g) in toluene (50 ml) at −78 °C. After 30 min, aqueous sodium hydroxide was added and the mixture allowed to warm to 20 °C. The separated organic layer was washed successively with dilute hydrochloric acid and brine, dried ($MgSO_4$), and evaporated to give a solid (0.5 g) which was recrystallised from methanol to give the *sulphoxide* (**4**) (0.27 g, 51%), m.p. 126—129 °C (Found: C, 69.1; H, 6.4; S, 12.2. $C_{15}H_{16}O_2S$ requires C, 69.2; H, 6.2; S, 12.3%); [^{1}H n.m.r. showed a mixture (*ca.* 4:1) of diastereoisomers, signals due to the major isomer are quoted here, see below for the minor isomer]; $\delta_H(CDCl_3)$ 2.75—3.05 (2 H, m, 2-H), 3.55 (1 H, br s, exch. D_2O), 4.1 (2 H, br s, $PhCH_2$), and 5.15—5.4 (1 H, m, 1-H).

(ii) A solution of the benzylthio alcohol (**1**) (0.4 g) and triethylamine (0.12 ml) in toluene (30 ml) was added dropwise to a stirred solution of NCS (0.22 g) in toluene (20 ml) at 0 °C. After 2 h, the reaction mixture was worked up as for (i) above to give an oily solid (0.4 g) which was recrystallised from methanol to give the sulphoxide (**4**) (0.26 g, 61%), m.p. 170—170.5 °C (^{1}H n.m.r. showed only one diastereoisomer); $\delta_H(CDCl_3)$ 2.78 (1 H, dd, *J* 12 and 1.5 Hz, 2a-H), 3.00 (1 H, dd, *J* 12.5 and 10 Hz, 2b-H), 3.73 (1 H, br s), 4.07 and 4.15 (2 H, ABq, *J* 12.5 Hz), 5.37 (1 H, dd, *J* 9.5 and 1.5 Hz, 1-H), and 7.25—7.43 (10 H, complex); δ_C[$(CD_3)_2SO$] 57 (t), 60 (t), 66 (d), 126 (d), 127 (d), 128 (d), 128.5 (d), 129 (d), 130 (d), 131 (s), and 144 (s).

Reaction of 2-Benzylthioacetophenone (**9**) *with* N-*Chlorosuccinimide.*—NCS (0.13 g) was added to a stirred solution of the ketone (**9**) (0.2 g) in toluene (30 ml) at 20 °C. After 1 h, the organic solution was washed successively with aqueous sodium hydroxide, dilute hydrochloric acid, and brine, dried ($MgSO_4$), and evaporated to give 2-benzylthio-2-chloroacetophenone (**5**) (0.21 g, 92% crude) as an opaque oil; $\delta_H(CCl_4)$ 3.76 and 4.0 (2 H, ABq, *J* 12 Hz), 5.95 (1 H, s), 7.0—7.5 (8 H, complex), and 7.6—7.9 (2 H, complex); the product was identified by comparison with material, lacking the signal at 5.95, derived from the α,α-dideuterio ketone.

Preparation of α-Benzylthio Ketones.—In a general procedure toluene-α-thiol (1 mol equiv.) was added dropwise to a stirred solution of the α-halogeno ketone and triethylamine (1 mol equiv.) in dry ether. The mixture was washed successively with dilute hydrochloric acid, aqueous sodium hydroxide, and brine, dried ($MgSO_4$), and evaporated to give the crude α-benzylthio ketone. 2-Benzylthioacetophenone (**9**),[19] 2-(benzylthio)acetone[20] (**10**), and 2-benzylthiocyclohexanone[21] (**12**) were known compounds. *2-Benzylthiopentan-3-one* (**11**) had b.p. 92 °C at 0.1 mmHg; $\delta_H(CDCl_3)$ 1.03 (3 H, t, *J* 7 Hz, 5-H), 1.36 (3 H, d, *J* 7 Hz, 1-H), 2.57 (2 H, m, 4-H), 3.3 (1 H, q, *J* 7 Hz, 2-H), 3.58 and 3.66 (2 H, ABq, *J* 13 Hz), and 7.2—7.31 (5 H, ArH) (Found: M^+, 208.0921. $C_{12}H_{16}OS$ requires *M*, 208.0922).

Alkylation of α-Benzylthio Ketones.—The α-benzylthio ketones were alkylated under the conditions specified in each case and, after standard work-up, products were purified as indicated.

Methylation of the ketone (**10**) (10 g): Sodium t-pentoxide (1 mol equiv.), C_6H_6 (42 ml), reflux 1 h; MeI (1.3 mol equiv.) 0—20 °C, 20 h gave *2-benzylthiobutan-2-one* (**15**) (96%), b.p. *ca.* 100 °C at 0.1 mmHg (Found: C, 67.75; H, 7.5. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.25%); $\delta_H(CDCl_3)$ 1.36 (3 H, d, *J* 7 Hz, 2.22 (3 H, s), 3.28 (1 H, q, *J* 7 Hz), 3.6 and 3.67 (2 H, ABq, *J* 13 Hz), and 7.23—7.32 (5 H, ArH).

Ethylation of the ketone (**15**) (1 g): NaH (1.15 mol equiv.), THF (30 ml), reflux 4 h, EtI (1.5 mol equiv.), reflux 40 h gave *3-benzylthio-3-methylpentan-2-one* (**16**), 61% after chromatography (Found: M^+, 222.1079. $C_{13}H_{18}OS$ requires *M*, 222.1078); $\delta_H(CDCl_3)$ 0.93 (3 H, t, *J* 7 Hz, 5-H), 1.41 (3 H, s, Me), 1.75 and 1.9 (2 H, d of ABq, *J* 14 and 7 Hz, 4-H), 2.28 (3 H, s, 1-H), 3.49 and 3.55 (2 H, ABq, *J* 12 Hz, $PhCH_2$), and 7.2—7.3 (5 H, ArH).

Ethylation of the ketone (**11**) (0.5 g): NaH (1.2 mol equiv.), THF (50 ml), reflux 30 min; EtI (2 mol equiv.), 25 °C, reflux 3 h gave 4-benzylthio-4-methylhexan-2-one (**17**), 76% after distillation; $\delta_H(CDCl_3)$ 0.98 (3 H, t, *J* 7.5 Hz, 1-H), 1.12 (3 H, t, *J* 7.5 Hz, 6-H), 1.49 (3 H, s, Me), 1.82 and 2.0 (2 H, d, of ABq, *J* 14 and 7 Hz, 2-H), 2.77 (2 H, m, 5-H), 3.53 and 3.59 (2 H, ABq, *J* 12 Hz, $PhCH_2$), and 7.26—7.38 (5 H, ArH); *m/z* 237 [$(M + 1)^+$, Cl], 179 (20%), 114 (15%), and 91 (100%).

Methylation of the ketone (**12**) (14.7 g): NaH (1.05 mol equiv.), THF (300 ml), reflux 40 min; MeI (1.5 mol equiv.), 20 °C, 17 h gave *2-benzylthio-2-methylcyclohexanone* (**18**), 95%, b.p. *c.a.* 100 °C at 0.1 mmHg (Found: C, 71.55; H, 7.8; S, 13.9. $C_{14}H_{18}OS$ requires C, 71.75; H, 7.75; S, 13.7%); $\delta_H(CDCl_3)$ 1.44 (3 H, s, Me), 1.55—1.73 (2 H, m), 1.75—1.9 (1 H, m), 1.92—2.17 (3 H, complex), 2.24 (1 H, dddd, *J* 14.5, 14.5, 2, and 2 Hz, 6_{eq}-H), 3.17 (1 H, ddd, *J* 14.5, 14.5, and 6 Hz, 6_{ax}-H), 3.39 and 3.68 (2 H, ABq, $PhCH_2$), and 7.22—7.31 (5 H, ArH).

Methylation of 2-benzylthioacetophenone (**9**) (2 g): NaH (1.15 mol equiv.), THF (70 ml), reflux 30 min; MeI (2 mol equiv.) 20 °C, 16 h gave 2-benzylthiopropiophenone (**13**);[22] $\delta_H(CCl_4)$ 1.5 (3 H, d, *J* 7 Hz, Me), 3.6 (2 H, br s, $PhCH_2$), 4.2 (1 H, q, *J* 7 Hz, 2′-H), 7.15 (5 H, $PhCH_2$), 7.1—7.5 (3 H), and 7.65—8.0 (2 H, Bz).

Methylation of the ketone (**13**) (1.4 g): NaH (1.2 mol equiv.), THF (35 ml), reflux 1 h; MeI (2 mol equiv.) 20 °C, reflux 1 h gave *2-benzylthio-2-methylpropiophenone* (**14**), 50% yield after chromatography, b.p. *ca.* 120 °C at 0.02 mmHg (Found: C, 75.35; H, 6.8; S, 12.1. $C_{17}H_{18}OS$ requires C, 75.5; H, 6.7; S, 11.85%); $\delta_H(CCl_4)$ 1.5 (6 H, s, Me_2C), 3.55 (2 H, s, $PhCH_2$), 7.05 (5 H, br s, $PhCH_2$), 7.0—7.5 (3 H), and 7.9—8.15 (2 H).

Reactions of α-Benzylthio Ketones with Organometallic Reagents.—Grignard reagents and methyl-lithium–lithium bromide were prepared by standard procedures. The lithium dimethylcopper–methyl-lithium reagent was prepared from methyl-lithium and copper(I) iodide.[23] Ethyl-lithium was prepared by slow addition of bromoethane in light petroleum (b.p. 30—40 °C) to washed lithium shot in light petroleum. The solvent was distilled off under reduced pressure and was gradually replaced by benzene; filtration gave the benzene solution of ethyl-lithium.[24]

Conditions used for the reactions are summarized in Table 2. Products were isolated by standard work-up procedures after quenching by addition of a small amount of water followed by aqueous HCl.

3-Benzylthio-3-methyl-2-phenylbutan-2-ol (**19**), b.p. *ca.* 120 °C at 0.02 mmHg (Found: C, 75.3; H, 7.55. $C_{18}H_{22}OS$ requires C, 75.5; H, 7.75%); $\delta_H(CDCl_3)$ 1.34 (3 H, s, Me_a of Me_2C), 1.43 (3 H, s, Me_b of Me_2C), 1.74 (3 H, s, 1-H), 2.98 (1 H, br s, OH), 3.52 (2 H, s, $PhCH_2$), and 7.15—7.7 (10 H, ArH).

(3RS,4RS)- *and* (3RS,4SR)-4-*Benzylthio*-3,4-*dimethylhexan*-3-*ol* (**20**) and (**21**) were obtained as a mixture, b.p. *ca.* 100 °C at 0.02 mmHg (Found: C, 71.55; H, 9.85; S, 12.95. $C_{15}H_{24}OS$ requires C, 71.4; H, 9.6; S, 12.7%); $\delta_H(CDCl_3)$ for (3*RS*,4*RS*)-isomer (**20**): 0.97 (3 H, t, *J* 7.5 Hz, $MeCH_2$) 1.09 (3 H, t, *J* 7.5 Hz, $MeCH_2$), 1.19 (3 H, s, MeCO), 1.26 (3 H, s, MeCS), 1.43—1.83 (4 H, complex, 2 × $MeCH_2$), 2.3 (1 H, br s, OH), 3.76 and 3.81 (2 H, ABq, *J* 12 Hz, $PhCH_2$), and 7.23—7.38 (5 H, ArH). For (3*RS*,4*SR*)-isomer (**21**): 0.95 and 1.09 (2 × 3 H, t, *J* 7.5 Hz, 2 × $MeCH_2$), 1.16 (3 H, s, MeCO), 1.29 (3 H, s, MeCS), 1.43—1.83 (4 H, complex, 2 × $MeCH_2$), 2.3 (1 H, br s, OH), 3.75 and 3.81 (2 H, ABq, *J* 12 Hz, $PhCH_2$), and 7.23—7.38 (5 H, ArH).

(1RS,2SR)-2-*Benzylthio*-1,2-*dimethylcyclohexanol* (**22**), b.p. *ca.* 100 °C at 0.02 mmHg (Found: C, 71.75; H, 8.75; S, 13.05. $C_{15}H_{22}OS$ requires C, 71.95; H, 8.85; S, 12.8%); $\delta_H(CDCl_3)$ 1.25 (3 H, s, 1-Me), 1.45 (3 H, s, 2-Me), 1.35—1.82 (7 H, complex), 2.01 (1 H, m), 2.45 (1 H, br s, OH), 3.82 (2 H, s, $PhCH_2$), and 7.2—7.37 (5 H, ArH).

(1RS,2RS)-2-*Benzylthio*-1,2-*dimethylcyclohexanol* (**23**), b.p. *ca.* 100 °C at 0.02 mmHg (Found: C, 71.9; H, 8.55. $C_{15}H_{22}OS$ requires C, 71.95; H, 8.85%); $\delta_H(CDCl_3)$ 1.35 (3 H, s, 1-Me), 1.46 (3 H, s, 2-Me), 1.44—1.95 (8 H, complex), 3.72 (2 H, s, $PhCH_2$), and 7.2—7.37 (5 H, ArH), This compound was identical with a sample prepared in the following way. Lithium hydride (13 mg) was added to a stirred solution of toluene-α-thiol (0.2 g) in DMF (15 ml) under nitrogen. The mixture was heated at 100 °C for 2 h. 1,6-Dimethyl-7-oxabicyclo[4.1.0]heptane (0.1 g) was added to the mixture, and stirring at 100 °C was continued for 42 h. After addition of aqueous HCl the product was isolated with light petroleum (washing with aqueous NaOH removed unchanged thiol). Chromatography on silica gel using ether–light petroleum (1:1) as eluant gave the β-benzylthio alcohol (50 mg, 22%).

β-Mercapto Alcohols.—β-Mercapto alcohols (**24**)—(**28**) were prepared by reduction of the β-benzylthio alcohols using the following general procedure: ammonia was condensed (acetone–solid CO_2) into a stirred solution of the β-benzylthio alcohol in a small quantity of dry ether (under nitrogen). Sodium was added in small pieces until a blue colour persisted for 20 min. A few crystals of ammonium chloride were then added to discharge the blue colour. The ammonia was evaporated under a flow of nitrogen. After addition of ether and extraction with sodium hydroxide (10%, × 2) the aqueous layers were acidified (aqueous HCl) and the product was isolated by extraction with ether (× 2) and dichloromethane. Having checked the n.m.r. spectrum, the crude product was used directly for formation of the 2-phenyl-1,3-oxathiolane. The following yields and n.m.r. data were obtained.

3-Mercapto-3-methyl-2-phenylbutan-2-ol (**24**) (89%); $\delta_H(CDCl_3)$ 1.31 (3 H, s, Me_a of Me_2C), 1.45 (3 H, s, Me_b of Me_2C), 1.73 (4 H, br s, 1-Me and SH), 2.64 (1 H, s, OH), and 7.2—7.7 (5 H, ArH).

(3RS,4RS)- *and* (3RS,4SR)-4-*Mercapto*-3,4-*dimethylhexan*-3-*ol* (**25**) and (**26**) (62%); $\delta_H(CDCl_3)$ for (3*RS*,4*RS*) (**25**): 0.99 (3 H, t, *J* 7.5 Hz, 1- or 6-H), 1.09 (3 H, t, *J* 7.5 Hz, 6- or 1-H), 1.18 (3 H, d, *J* 1 Hz, MeCOH), 1.3 (3 H, d, *J* 1 Hz, MeCSH), 1.34 (1 H, br s, SH), 1.39—1.56 (1 H, m, $MeCH_aH_b$), 1.58—1.77 (3 H, complex, $MeCH_2$ and $MeCH_aH_b$), and 2.17 (1 H, br s, OH). For (3*RS*,4*SR*) (**26**): 0.98 (3 H, t, *J* 7.5 Hz, 1- or 6-H), 1.09 (3 H, t, 7.5 Hz, 6- or 1-H), 1.17 (3 H, d, *J* 1 Hz, MeCOH), 1.32 (3 H, br s, MeCSH), 1.39—1.56 (1 H, m, $MeCH_aH_b$), 1.58—1.77 (3 H, complex, $MeCH_2$ and $MeCH_aH_b$), and 2.17 (1 H, br s, OH). The ratio of (**25**):(**26**) correlated with the ratio of (**20**):(**21**) in the starting material for different initial ratios.

(1RS,2SR)- *and* (1RS,2RS)-2-*Mercapto*-1,2-*dimethylcyclohexanol* (**27**) and (**28**) (82%) (Found: C, 59.75; H, 10.2; S, 20.1. $C_8H_{16}OS$ requires C, 59.95; H, 10.05; S, 20.0%); $\delta_H(CDCl_3)$ for (1*RS*,2*SR*) (**27**): 1.24 (3 H, s, MeCOH), 1.44 (3 H, s, MeCS), 1.38—1.76 (7 H, complex), 1.67 (1 H, s, SH), 1.9—2.03 (1 H, m), and 2.17 (1 H, br s, OH). For (1*RS*,2*RS*) (**28**): 1.38 (3 H, s, MeCOH), 1.45 (3 H, s, SH), 1.38—2.03 (8 H, complex), 1.62 (1 H, s SH), and 2.15 (1 H, br s, OH).

2-Phenyl-1,3-oxathiolanes.—The oxathiolanes (**29**)—(**32**) were prepared by the following general procedure. Toluene-*p*-sulphonic acid (*ca.* 0.005 mol equiv.) and an excess of freshly distilled benzaldehyde were added to a stirred solution of the β-mercapto alcohol in dry benzene. The mixture was refluxed under nitrogen until no spot corresponding to starting material was observed on t.l.c. Evaporation of the benzene and benzaldehyde gave the crude product. The following data were obtained.

4,4,5-*Trimethyl*-2,5-*diphenyl*-1,3-*oxathiolane* (**29**); $\delta_H(CDCl_3)$ (major diastereoisomer italicised) *1.1* and 1.13 (3 H, s), 1.54 and *1.59* (3 H, s), 1.9 (3 H, s), *6.3* and 6.56 (1 H, s PhCH), and 7.25—7.6 (10 H, ArH); *m/z* 285 [$(M + 1)^+$, Cl].

4,5-*Diethyl*-4,5-*dimethyl*-2-*phenyl*-1,3-*oxathiolane* (**30**) and (**31**), b.p. *ca.* 110 °C at 0.02 mmHg; $\delta_H(CDCl_3)$ (mixture of 4-diastereoisomers) 1.0—2.0 (15.5 H, complex), 2.32 (0.5 H, m), 5.95 (0.5 H, s, 2-H), 6.03 (0.5 H, s, 2-H), and 7.27—7.52 (5 H, ArH) (Found: M^+, 250.1391. $C_{15}H_{22}OS$ requires *M*, 250.1391).

(1RS,6SR,8RS)- *and* (1RS,6SR,8SR)-1,6-*Dimethyl*-7-*oxa*-8-*phenyl*-9-*thiabicyclo*[4.3.0]*nonane* (**32**) (assignment of stereo-

chemistry of the two diastereoisomers is based on an n.O.e experiment), m.p. *ca.* 20 °C (Found: C, 72.3; H, 8.1; S, 12.65. $C_{15}H_{20}OS$ requires C, 72.55; H, 8.1; S, 12.9%); $\delta_H(CDCl_3)$ for (1*RS*,6*SR*,8*RS*): 1.43 (3 H, s, Me), 1.44 (3 H, s, Me), 1.28—1.9 (6 H, complex), 2.15—2.32 (2 H, complex), 6.23 (1 H, s, 8-H), 7.26—7.42 (3 H, complex, ArH), and 7.47—7.55 (2 H, complex, ArH). For (1*RS*,6*SR*,8*SR*): 1.38 (3 H, s, Me), 1.47 (3 H, s, Me), 1.28—1.9 (6 H, complex), 2.0—2.32 (2 H, complex), 6.15 (1 H, s, 8-H), 7.26—7.42 (3 H, complex, ArH), and 7.47—7.55 (2 H, complex, ArH).

Preparation of Olefins from 2-Phenyl-1,3-oxathiolanes.—General procedure: butyl-lithium (*ca.* 1.5M) was added dropwise under nitrogen to a stirred solution of di-isopropylamine (1.5 mol equiv. relative to BuLi) in dry ether (half of total volume used) at 0 °C. The mixture was stirred under a slow flow of nitrogen for 15 min. A solution of the oxathiolane and the g.l.c. standard (where used) in dry ether (remainder) was added to the stirred solution of the base at 20 °C. After the specified time a small amount of water was added, and the ethereal solution was washed successively with aqueous NaOH, aqueous HCl, and brine. Products were analysed by g.l.c. and/or by evaporation of the dried solution and subsequent n.m.r. examination. A Carlo Erba capillary g.c. 2151 instrument using an OV 101 capillary column (WCOT, 50 m) was used for g.l.c.

2-Methyl-3-phenylbut-2-ene (**33**) was obtained in 75% crude yield from oxathiolane (**29**) (95 mg) using LDA (5 mol equiv.) in ether (5 ml) for 9 h. The n.m.r. spectrum was in agreement with that in the literature.[25]

(E)- *and* (Z)-*3,4-Dimethylhex-3-ene* (**34**) and (**35**) were prepared from two different mixtures of the oxathiolanes (**30**) and (**31**). One mixture, (**30**):(**31**) = 0.6 (47 mg) with LDA (3 mol equiv.) in ether (4 ml) for 9 h gave a 98% (g.l.c.) yield of compounds (**34**) and (**35**) in the ratio 0.6. Similarly another mixture, (**30**):(**31**) = 2.1 (32 mg) with LDA (8 mol equiv.) in ether (5 ml) for 11 h gave a 100% (g.l.c.) yield of compounds (**34**) and (**35**) in the ratio 2.1. 1-Methylcycloheptene (R_t 39 min) was used as internal standard at 35 °C and the R_ts for (*E*)- (**34**) and (*Z*)-isomer (**35**) were 27 and 28 min, respectively. The (*E*)- and (*Z*)-olefins (**34**) and (**35**) were identified by comparison with authentic material obtained by Eastwood's procedure[26] from the diastereoisomeric 3,4-dimethylhexane-3,4-diols in the light of the literature assignments.[17,18]

1,2-Dimethylcyclohexene (**36**) was obtained in 92% yield (g.l.c.) from the oxathiolane (**32**) (125 mg) using LDA (5 mol equiv.) in ether (6 ml) for 8 h. 1,2,4-Trimethylbenzene (R_t 38 min) was used as internal standard at 40—70 °C (programmed); under these conditions the olefin (**36**) had an R_t of 28 min. The n.m.r. spectrum of the olefin (**36**) was compatible with that in the literature.[26]

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