Rearrangements of 2-Phenylthioethanols with Alkenyl, Alkynyl, Ester, and Other Functionalised Alkyl Substituents at the Migration Origin: Synthesis of γ-Phenylthiocrotonate Esters

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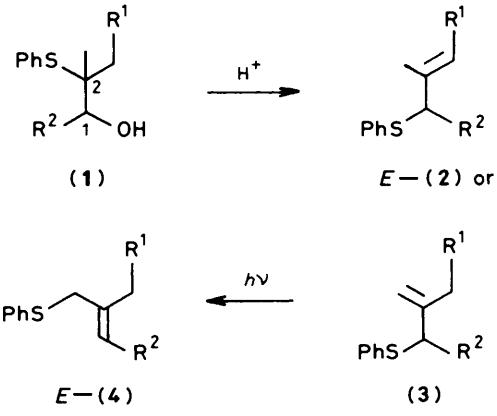
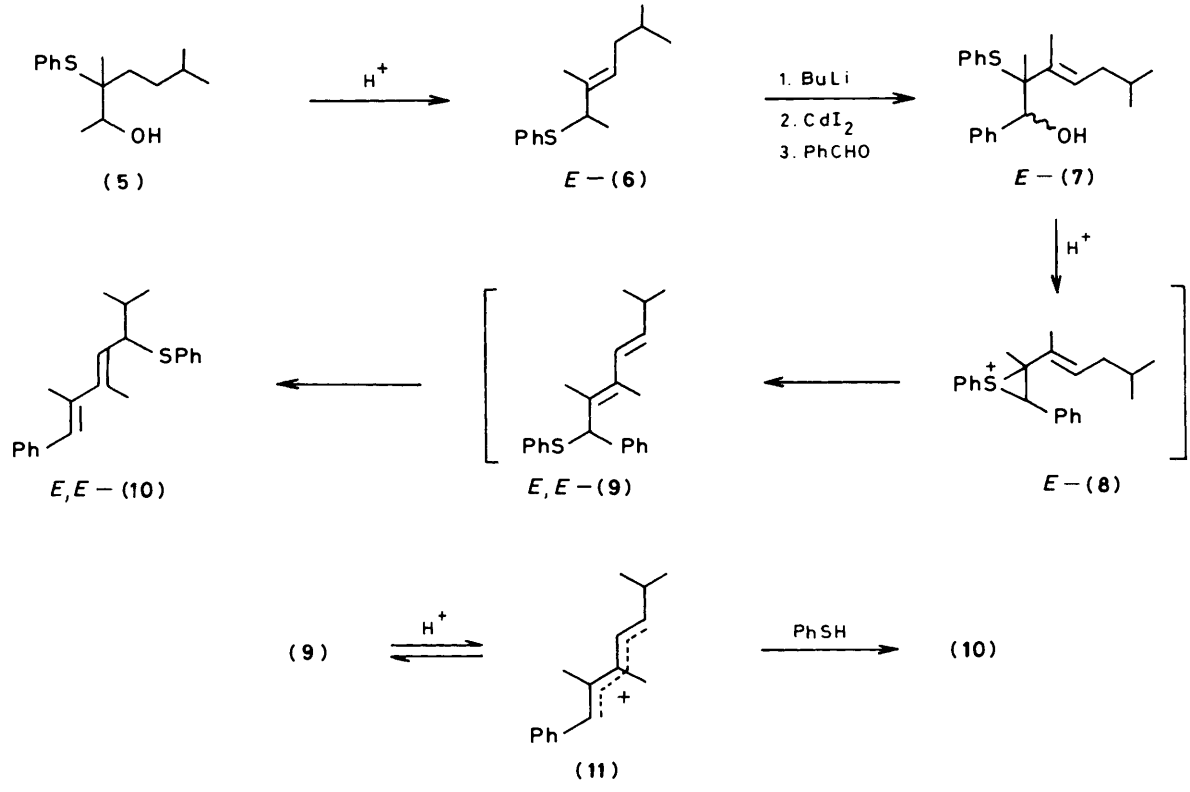
The effects of functional groups near the migration origin in [1,2] and [1,3] PhS shifts are explored: an α-CO_2R group prevents migration, α or β vinyl groups have only steric effects, alkynyl or CO_2Et groups encourage rearrangement and provide routes to γ-phenylthio unsaturated esters and ketones.

Rearrangements[1,2] of 2-phenylthio (PhS) ethanols (**1**) provide a route to allyl sulphides (**2**) or (**3**) or, by a photochemical [1,3] PhS shift,[3] their isomers (**4**). The products may be used directly to prepare allylic alcohols, by the Evans-Mislow rearrangement,[4] or as anions in the construction of further carbon–carbon bonds [*e.g.* (**6**) to (**7**)]. We now describe the effects of functional groups (alkenyl, alkynyl, vinyl chloride, CN, and CO_2R) in the alkyl chain attached to the migration origin [R^1CH_2 on C-2 in (**1**)]. The functional groups may encourage or prevent the rearrangement, may affect the position [(**2**) *vs.* (**3**)] or geometry [*E*-(**2**) *vs.* *Z*-(**2**)] of the new double bond, and may even generate new functionality as a result of migration. We have already reported the effects of a second PhS group[5] or a diphenylphosphinoyl (Ph_2PO) group[6] on the rearrangement.



(**1**) *E*—(**2**) or *E*—(**4**) (**3**)

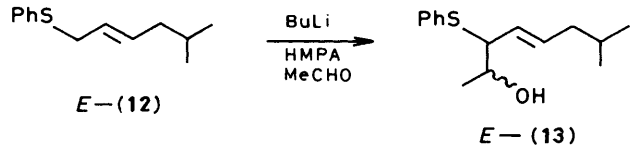
A double bond in the side chain might encourage rearrangement if it were able to conjugate with the developing cation at the migration origin [R^1CH_2 = alkenyl in (**1**)]. Thus the allyl sulphide (**6**), prepared by rearrangement of the alcohol (**5**), formed an allylic anion which added benzaldehyde to give only the α-product (**7**). Rearrangement in acid gave a moderate yield of the diene (**10**) presumably *via* the episulphonium ion (**8**) and a [1,5] PhS shift (or two successive [1,3] PhS shifts), on the intermediate diene (**9**). The [1,5] shift cannot be prevented by working in the dark and is presumably acid-catalysed like other



(**5**) *E*—(**6**) *E*—(**7**) *E*—(**8**) *E,E*—(**9**) *E,E*—(**10**) (**11**)

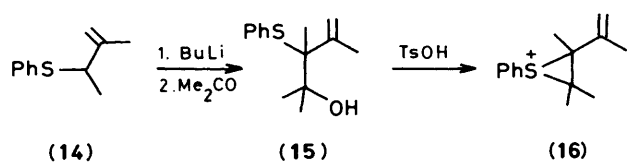
[1,3] PhS shifts[3] where a benzylic cation [here (**11**)] is an intermediate.

PhS migrations from a secondary migration origin to a secondary migration terminus occur if the developing cation can be stabilised by a C–Si bond.[7] We hoped that an alkenyl group might similarly encourage the alcohol (**13**) to rearrange but no products were isolated from attempted acid-catalysed rearrangements (TsOH, toluene or P_2O_5, benzene) though the alcohol (**13**) rapidly disappeared. An attempted base-catalysed rearrangement (MsCl, Et_3N) gave a small yield of a chloride (perhaps rearranged) identified only by its mass spectrum (*m/z* 268/270).

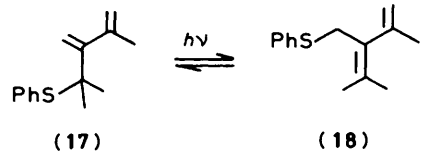


E–(**12**) *E*–(**13**)

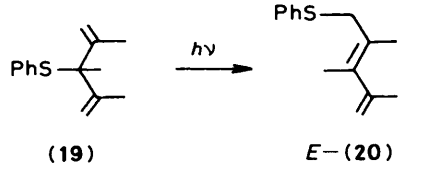
The tertiary alcohol (**15**) dehydrated in acid to give rearranged (17) and unrearranged (**19**) allyl sulphides in about equal amounts, both *via* the episulphonium ion (**16**). The symmetrical unconjugated diene (**19**) gave the conjugated diene



(**14**) (**15**) (**16**)



(**17**) (**18**)

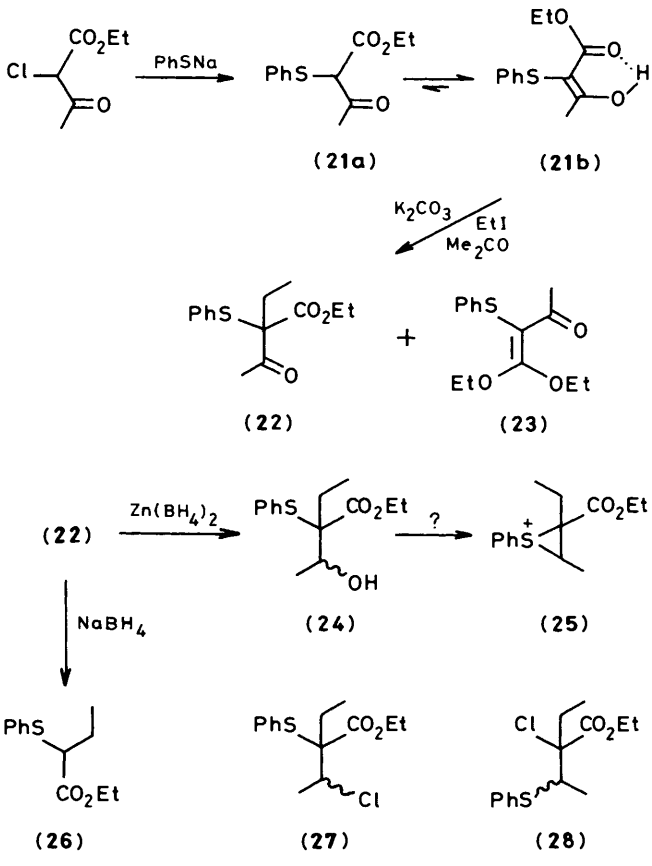


(**19**) *E*–(**20**)

(**20**) on photochemical [1,3] PhS shift, but the conjugated diene (**17**) gave a mixture of (**17**) and (**18**) on exposure to light. Developing conjugation is not enough to drive the [1,2] PhS shift but is enough to drive the [1,3] PhS shift [(**19**) to (**20**)] to completion.

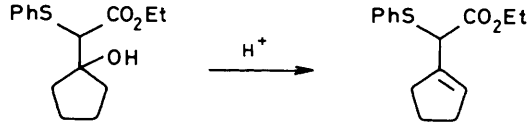
We hoped that a carbonyl group at the migration origin might not prevent the formation of an episulphonium ion [*e.g.* (**25**)] and hence might allow elimination with rearrangement. The phenylthioacetoacetate (**21**) (which was 92% enol by n.m.r., with the enol proton at δ 13.8) gave an unreactive sodium enolate in tetrahydrofuran (THF). In ethanol with K_2CO_3 a reverse Claisen ester condensation occurred (we have similarly fragmented a cyclic phenylthio keto ester[8]), but in acetone with K_2CO_3 and ethyl iodide ethylation occurred giving 60—65% *C*-ethyl product (**22**) and a low yield of *O*-ethyl product (**23**) which rearranged to (**22**) with time and was hydrolysed to (**21**) in dilute acid.

Reduction of keto ester (**22**) with sodium borohydride or



(**21a**) (**21b**) (**22**) (**23**) (**24**) (**25**) (**26**) (**27**) (**28**)

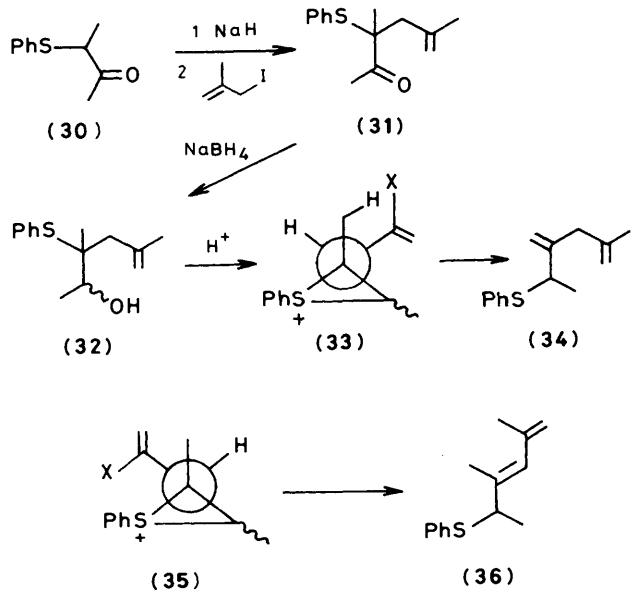
$LiAlH(OBu^t)_3$ gave the reverse aldol products (**26**) but zinc borohydride[9] gave the required alcohol (**24**) in good yield. Attempted acid-catalysed rearrangement (TsOH, toluene or P_2O_5, benzene) again gave the reverse aldol product (**26**), and base-catalysed rearrangement ($SOCl_2$, pyridine or MsCl, Et_3N) gave a mixture of unrearranged (**27**) and rearranged (**28**) chlorides which did not eliminate HCl on treatment with NaOEt or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). Evidently the episulphonium ion (**25**) can be formed but the carbonyl group does not sufficiently promote elimination or nucleophilic substitution to give rearranged products in useful yields. Attempted protection of ketones (**21**) or (**22**) with ethanediol in acid solution led only to decomposition. The tertiary alcohol (**29**) has been reported[10] to dehydrate (TsOH, benzene) without rearrangement.



(**29**)

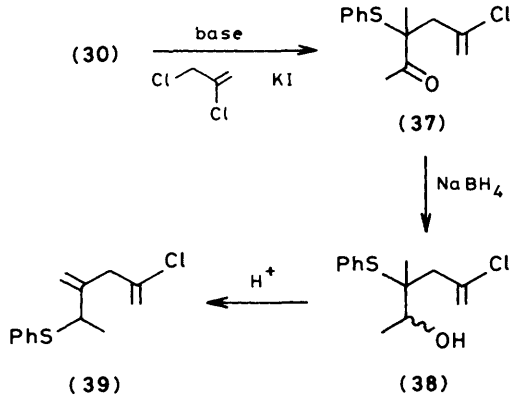
Allylic Substituents.—Unsaturation at the next carbon atom along the same chain could promote rearrangement by conjugation with the developing double bond. We have explored carbon–carbon double and triple bonds, and the vinyl chloride, nitrile, and ester functionalities in this position.

Alkylation of the α-phenylthio ketone (**30**) with methylallyl iodide and reduction of the product (**31**) gave the unsaturated alcohol (**32**) which rearranged in acid (P_2O_5, toluene, or TsOH, benzene, or TsOH, MeCN) in high yield to the *exo* methylene



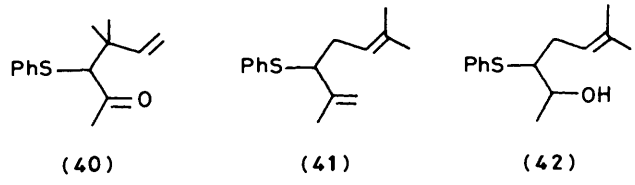
compound (**34**). This unusual result—the double bond is normally[1] formed in the longer chain, *cf.* (**6**), even without conjugation—may have a steric explanation: the episulphonium ion (**35**; X = Me) required for elimination to give the conjugated diene (**36**) has bad steric interactions absent in the episulphonium ion (**33**; X = Me) leading to (**34**). We have found[2] similar relationships between stereochemistry and regioselectivity of eliminations in the rearrangement of cyclic analogues of (**1**).

Alkylation of the same α-phenylthio ketone (**30**) with 2,3-dichloropropene and reduction of the product (**37**) gave the alcohol (**38**) which rearranged to the analogous unconjugated diene (**39**). Presumably the episulphonium ion (**35**; X = Cl) is again unfavourable. Attempts to isomerise (**39**) to a conjugated diene or to hydrolyse the vinyl chloride[11] to a ketone in either (**38**) or (**39**) failed.

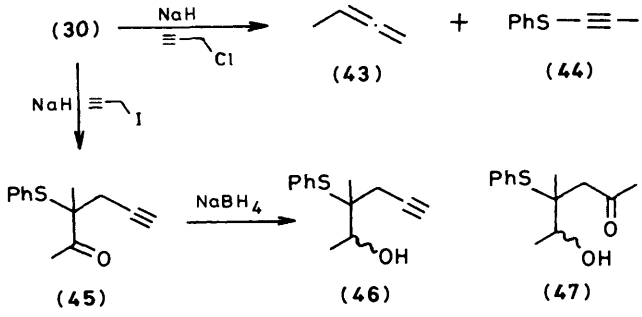


A dimethylallyl (prenyl) group was not enough to drive a secondary to secondary PhS migration. Prenylation of phenylthio acetone gave some allylic inversion (**40**) but mostly the required ketone (**41**) which was reduced to the alcohol (**42**). Rearrangement in acid (TsOH or P_2O_5 in toluene) gave no recognisable products, as in the rearrangement of the analogous alcohol (**13**). Presumably any products are unstable under the reaction conditions.

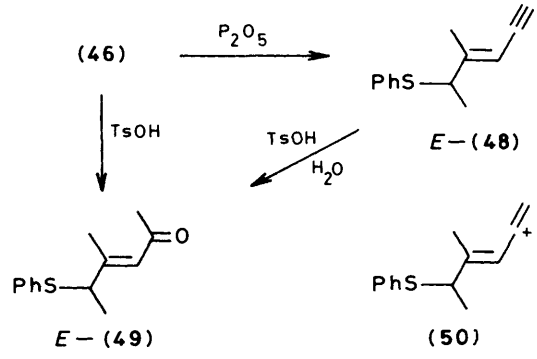
We hoped to introduce a ketone into the rearranging



molecule and the problems with compounds such as (**32**) and (**38**) suggested that an alkyne would be an ideal masked ketone. It would lack the steric bulk of the branched alkenyl groups, could be hydrated to give the ketone before or after rearrangement, and the reduction of the intermediate (**45**) would present no chemoselectivity problems.



Attempted alkylation of the α-phenylthio ketone (**30**) with prop-2-ynyl chloride gave a mixture of (**43**) and (**44**). Prop-2-ynyl iodide gave an acceptable yield (60%) of the ketone (**45**) with some (**43**) and (**44**). Reduction gave the alcohol (**46**) but all attempts to hydrate the triple bond to form the keto alcohol (**47**) failed, perhaps because the soft Lewis acids, *e.g.* Hg^{II}, used to attack the triple bond, attack PhS even more readily.



Rearrangement of the alcohol (**46**) under dehydrating conditions (P_2O_5 in benzene or toluene) gave the conjugated enyne *E*-(**48**) and no *exo*-methylene compound. The smaller ethynyl group must fit into an episulphonium ion analogous to (**35**), or the reaction must be under thermodynamic control. Rearrangement of (**46**) with TsOH in benzene gave the product of rearrangement *and hydration*, the conjugated γ-phenylthio enone (**49**) as a 4:1 *E*:*Z* mixture. Water is available from the alcohol (**46**) and from the water of crystallisation of TsOH. Treatment of the enyne (**48**) under the same conditions also gave the enone (**49**). Hydration of enynes commonly occurs without Lewis acid catalysts as the vinyl cation, here (**50**), is stabilised by conjugation.[12]

Alkylation of the same α-phenylthio ketone (**30**) with 1-bromopent-2-yne, prepared from prop-2-ynyl alcohol by alkylation[13]

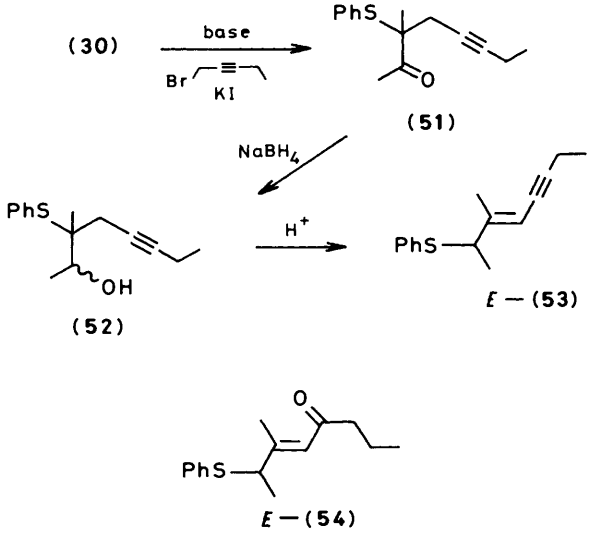
Table. Rearrangement of lactones (**63**)

Starting material				Product		
Compd.	R^1	R^2	ROH	Compd.	Yield (%)	Stereo
(**63a**)	H	H	EtOH	(**65a**; R = Et)	74	*E*
(**63b**)	H	Me	MeOH	(**65b**; R = Me)	64	*E*
			EtOH	(**65b**; R = Et)	88	*E*
			BuOH	(**65b**; R = Bu)[a]	85	*E*
(**63c**)	H	Bu^t	MeOH		*b*	—
(**63d**)	Me	H	MeOH	(**65e**; R = Me)	60	Mixture
(**63e**)	Et	H	MeOH	(**65e**; R = Me)[c]	84	4:3
			BuOH	(**65e**; R = Bu)[d]	80	1:1, *E*:*Z*[e]
				(**66e**; R = Bu)[d]		4:3, *E*:*Z*[e]
(**63f**)	Pr^i	H	MeOH	(**70**)	83	—
(**63g**)	Ph	H	MeOH	(**65g**; R = Me)	87	3:2
(**63h**)	Me	Me	MeOH	(**65h**; R = Me)	81	4:1, *E*:*Z*
			BuOH	(**65h**; R = Bu)	75	6:1, *E*:*Z*
(**63i**)	Et	Me	EtOH	(**65i**; R = Et)[f]	64	5:1, *E*:*Z*
			BuOH	(**65i**; R = Bu)[f]	49	5:1, *E*:*Z*

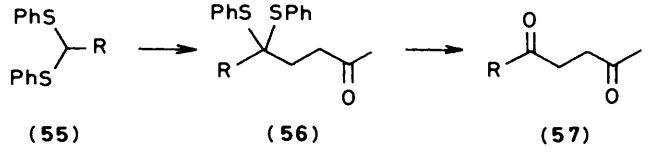
[a] After 24 h, 1:1 mixture of (**65b**) and (**72**); after 48 h, only (**65b**) remains. [b] Decomposes under reaction conditions. [c] At first, some (**66e**) is present, but after 6 days only (**65e**) remains. [d] Not separated. [e] Stereochemistry assigned after hydrolysis to the acids (**65e**; R = H) and (**66e**; R = H). [f] Containing *ca.* 20% (**66i**).

and substitution, gave the ketone (**51**) with no by-products and reduction gave the alcohol (**52**). Rearrangement of this alcohol (**52**) under either set of conditions gave the conjugated enyne (**53**) which was not hydrated to the expected ketone (**54**) with TsOH, but decomposed instead.

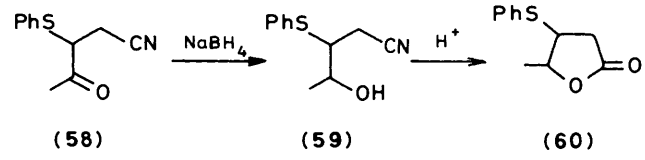
Some alternative routes to γ-phenylthio enones were briefly explored. Addition of the lithium derivative of the bis(phenylthio)acetal[5] (**55**; R = Ph), or of the cuprate[14] derived from it, to butenone gave good yields of the Michael adduct (**56**; R = Ph). Attempted formation of the monosulphoxide of (**56**; R = Ph),

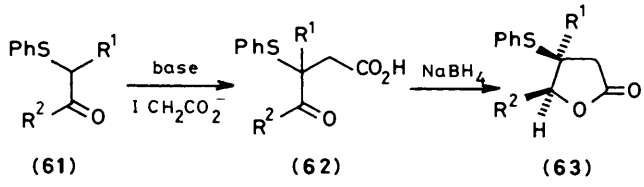


which might have eliminated PhSOH to give a γ-phenylthio enone, gave instead a good yield of the 1,4-diketone (**57**; R = Ph). Addition of (**55**; R = Pr^i) or of the monosulphide of (**55**; R = Pr^i) to butenone was unsuccessful.



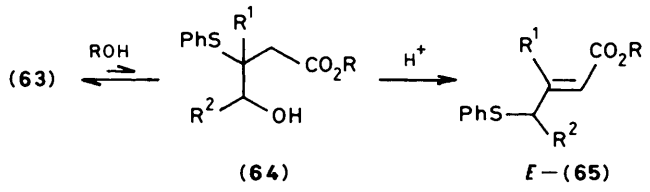
Nitriles and Esters.—The nitrile (**59**) was prepared by alkylation of phenylthio acetone and reduction of the product (**58**), but treatment with acid gave the lactone (**60**) without rearrangement. We have already described[5] the regioselective synthesis of α-phenylthio ketones (**61**), their alkylation[15] to give keto acids (**62**), and their reduction[15] to give the lactones (**63**). These lactones (**63**) do not rearrange under the usual conditions (TsOH, benzene or toluene), presumably because the PhS group cannot execute the 6-*endo-tet* displacement of the carboxylic acid required for participation.





Treatment of the lactones (**63**) with TsOH in benzene or toluene containing an alcohol (MeOH, EtOH, or BuOH) successfully induced rearrangement[16] to the γ-phenylthiocrotonate esters (**65**) (Table). These rearrangements are very slow, requiring 2—6 days refluxing, and presumably occur by unfavourable ester exchange to give a very small proportion of the open chain compound (**64**) which can rearrange in the usual way.

The simplest PhS migration from a tertiary migration origin to a secondary migration terminus (**63h**) occurred in high yield giving mostly *E*-(**65h**) and no *exo*-methylene compound. Even with an ethyl group at the migration origin (**63i**) only a small proportion of the non-conjugated product (**66**; R^2 = Me) was formed. Comparison with allylic substituents in (**32**) and (**38**) shows that the ester group is successful in attracting the newly formed double bond with conjugation, either by thermo-

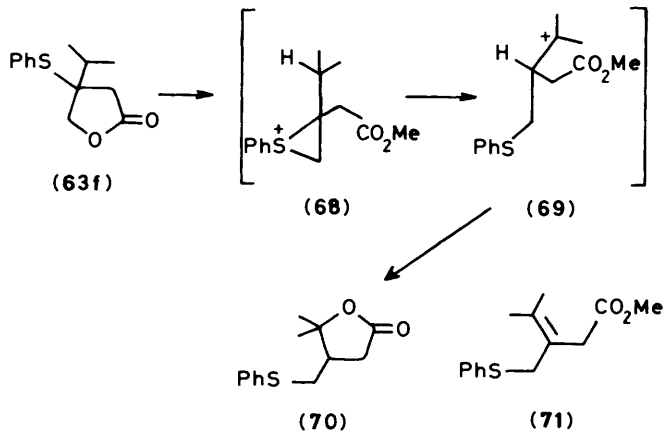


(64) E-(65)

(66) (67)

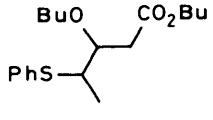
dynamic control, or by making the proton H^A more acidic in the episulphonium ion intermediate (**67**).

Tertiary to primary PhS migration was also successful, with straightforward results for (**63d**) and (**63g**). With R^1 = Et (**63e**), some non-conjugated product (**66**; R^2 = H) was formed but prolonged heating in methanol converted this into the conjugated product (**65e**). These compounds (**65d,e,g**) were formed as mixtures of geometrical isomers whose configuration was not assigned. One tertiary to primary rearrangement gave an unexpected result as (**63f**) gave a new γ-lactone (**70**) in good yield, presumably *via* intermediates (**68**) and (**69**), which are perhaps in equilibrium with (**65f**) and (**71**).



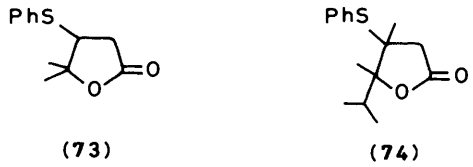
(63f) (68) (69) (70) (71)

The influence of the ester group was clearly seen in a successful PhS migration from a secondary to secondary centre (**63b**) giving an excellent yield of *E*-(**65b**). In butanol, the butyl ether (**72**) was formed in the early stages but prolonged heating converted this into (**65b**), presumably *via* return to the episulphonium ion (**67b**). Even a secondary to primary PhS migration occurred in good yield to give (**65a**), the known product of PhS^- attack on ethyl γ-bromocrotonate.



(72)

Compounds with tertiary alkyl groups were alone unsatisfactory. The t-butyl compound (**63i**) decomposed under the reaction conditions and the tertiary alkyl esters (**73**) and (**74**)



(73) (74)

gave diphenyl disulphide as the only recognisable organic product.

Developing conjugation with a carbonyl group encourages the [1,2] PhS shift but not the [1,3] PhS shift,[17] whilst developing conjugation with a carbon–carbon double bond encourages the [1,3] but not the [1,2] shift. Regiospecific synthesis of α-phenylthio ketones,[4] alkylation, reduction, and rearrangement is a suitable synthesis for a wide variety of γ-phenylthio unsaturated carbonyl compounds. The γ-phenylthio crotonates are available by other routes involving [1,3] PhS shifts[18] and we have studied reactions of the extended enolate anions derived from them.[19]

Experimental

General procedures have been described elsewhere.[15] T.l.c. solvents were: (A) acetone (30%)–light petroleum (b.p. 60—80 °C); (B) ether (20%)–light petroleum (b.p. 30—40 °C); (C) ether (50%)–light petroleum (b.p. 30—40 °C).

2,3,6-*Trimethyl*-1-*phenyl*-5-*phenylthiohepta*-1,3-*diene* (**10**).—In a foil-wrapped flask, the alcohol[1a] (**7**) (45 mg), toluene-*p*-sulphonic acid (10 mg), and dry benzene (4 ml) were heated under reflux for 45 min; aqueous sodium hydrogen carbonate was then added and the mixture extracted with dichloromethane (3 × 15 ml). The extracts were dried (Na_2SO_4), evaporated, and subjected to preparative t.l.c. to give the *diene* (23 mg, 54%), R_F (A) 0.65, $\nu_{max.}$(film) 1 597 cm^{-1} (C=C), a mixture of geometric and diastereoisomers; δ($CDCl_3$) 7.0—7.6 (5 H, m, Ph), 6.70 and 6.49 (1 H, each s, PhC*H*=CH), 5.4—5.9 (1 H, m, C=C*H*CHS), 3.8—4.0 (1 H, m, C=CHC*H*SPh), and 0.8—2.2 (13 H, m, other protons); *m/z* 322 (M^+, 6%), 232 (21), 218 (23), 213 (25), 169 (38), 155 (32), 110 (100), and 69 (49) (Found: M^+, 322.1737. $C_{22}H_{26}S$ requires *M*, 322.1754).

Attempted Rearrangement of the Homoallyl Alcohol (**13**).—The alcohol[1b] reacted rapidly with toluene-*p*-sulphonic acid in benzene or toluene at reflux or phosphorus pentaoxide in toluene at reflux, but did not give an identifiable product. With methanesulphonyl chloride (excess) in triethylamine (0.2 ml) and dichloromethane (4 ml) for 6 h, the alcohol (40 mg) gave, after preparative t.l.c., the corresponding (or a rearranged) chloride (17 mg, 40%), R_F (A) 0.64, *m/z* 268/270 (M^+), and 233 (*M* − Cl, 100%).

Dehydration of the Alcohol (**15**).—In a foil-wrapped flask, the alcohol[1a] (0.29 g), toluene-*p*-sulphonic acid (45 mg), and dry benzene (30 ml) were heated under reflux for 20 min, sodium hydrogen carbonate solution was added, the benzene layer was separated, and the aqueous layer extracted with dichloromethane (2 × 10 ml). The combined organic fractions were dried (Na_2SO_4) and evaporated to give a 5:4 mixture (0.22 g, 82%) of 3-methyl-2-(1-methyl-1-phenylthioethyl)buta-1,3-diene (**17**) and 2,3,4-trimethyl-3-phenylthiopenta-1,4-diene (**19**), R_F (A) 0.70, δ($CDCl_3$) 7.1—7.6 (5 H, m, Ph), 4.5—5.2 (4 H, m, $C=CH_2$), 1.82 [3 H for (**17**), 6 H for (**19**), m, *Me*C=CH_2], 1.43 [3 H, s, MeCS of (**19**)], and 1.40 [6 H, s, Me_2CS of (**17**)]. On exposure to sunlight, (**19**) isomerized completely to 2,3,4-trimethyl-5-phenylthiopenta-1,3-diene (**20**), whilst *ca.* 75% of (**17**) isomerized to 2,4-dimethyl-3-(phenylthiomethyl)penta-

1,3-diene (**18**). The mixture, R_F (A) 0.70, and (**20**) was a mixture of *E* and *Z* isomers (3:2); δ($CDCl_3$) 7.1—7.6 (5 H, m, Ph), 4.5—5.2 (2 H, m, C=CH_2), 3.68 *Z*-(**20**), 3.65 (**18**), and 6.44 *E*-(**20**) (2 H, each s, SCH_2), and 1.5—1.8 (9 H, 5 lines, MeC=C).

Ethyl 3-Oxo-2-phenylthiobutanoate (**21**).—Thiophenol (6.6 g) and sodium hydroxide (2.4 g) were stirred in absolute ethanol (25 ml) until the alkali dissolved (1.5 h). The sodium thiophenoxide solution was added dropwise to ethyl 2-chloroacetoacetate (9.9 g) in ethanol (50 ml). The extracts were dried ($MgSO_4$) and evaporated, and passed down a column of silica with dichloromethane–carbon tetrachloride (1:1) as eluant to give ethyl 2-phenylthioacetoacetate[20] (10.2 g, 72%), a mixture of the keto form (**21a**) and the enol form *E*-(**21b**) (8:92), R_F (A) 0.57, $\nu_{max.}$(film) 3 300—2 500 (enol OH) 1 734, 1 721, 1 632, and 1 599 cm^{-1} (C=O and enol C=C); δ($CDCl_3$) 13.82 (1 H, s, OH of enol), 7.0—7.4 (5 H, m, Ph), 4.20 (2 H, q, *J* 7 Hz, CO_2CH_2Me), 3.73 (1 H, s, SCH of keto form), 2.32 (3 H, s, COMe and MeC=C), and 1.16 (3 H, t, *J* 7 Hz, CO_2CH_2Me); *m/z* 238 (M^+, 39%), 192 (39), 150 (45), 121 (40), 110 (31), and 43 (100).

Alkylation of (**21**) *with Ethyl Iodide.*—(a) *With sodium hydride in THF.* The sodium enolate of (**21**) (from NAH) in THF did not react with ethyl iodide (25 h at reflux).

(b) *With potassium carbonate in ethanol.* AnalaR K_2CO_3 (0.5 g), (**21**) (0.42 g), and absolute ethanol (20 ml) were heated under reflux for 0.5 h, after which ethyl iodide (0.15 ml) was added and heating continued for 1.5 h. The ethanol was removed under reduced pressure, the residue was extracted with chloroform, and the extracts were dried (Na_2SO_4), evaporated, and subjected to preparative t.l.c. to give ethyl phenylthioacetate[21] (0.27 g, 66%), R_F (A) 0.44, $\nu_{max.}$(film) 1 734 cm^{-1} (C=O); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 4.10 (2 H, q, *J* 7 Hz, CO_2CH_2Me), 3.57 (2 H, s, CH_2), and 1.16 (3 H, t, *J* 7 Hz, CO_2CH_2Me); *m/z* 196 (M^+, 26%), 123 (39), 110 (26), 73 (100), and 59 (26).

(c) *With potassium carbonate in acetone.* Under nitrogen, (**21**) (4.0 g), AnalaR K_2CO_3 (3.0 g), ethyl iodide (1.4 ml), and dry acetone (100 ml) were heated under reflux for 40 h. Work-up as for (b) gave an oil which when passed down a column of silica with dichloromethane as eluant to give ethyl 2-ethyl-3-oxo-2-phenylthiobutanoate (**22**) (2.62 g, 59%), R_F (A) 0.36, (CH_2Cl_2) 0.63, $\nu_{max.}$(film) 1 737 (ester C=O) and 1 710 cm^{-1} (ketone C=O); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 4.25 (2 H, q, *J* 7 Hz, CO_2CH_2Me), 2.33 (3 H, s, COMe), 1.6—2.1 (2 H, m, SCH^*_2Me), 1.28 (3 H, t, *J* 7 Hz, CO_2CH_2Me), and 1.00 (3 H, t, *J* 7.5 Hz, SCH_2Me); *m/z* 266 (M^+, 54%), 224 (100), 223 (31), 178 (61), 149 (55), 109 (49), and 43 (89); the *semicarbazone* had m.p. 153.5—154 °C (from ethanol) (Found: C, 55.8; H, 6.6; N, 13.2; S, 9.8. $C_{15}H_{21}N_3O_3S$ requires C, 55.7; H, 6.6; N, 13.0; S, 9.9%); and 4,4-diethoxy-3-phenylthiobut-3-en-2-one (**23**) (0.12 g, 3%), R_F (A) 0.33, R_F (CH_2Cl_2) 0.46, δ($CDCl_3$) 7.0—7.3 (5 H, m, Ph), 4.09 (2 H, q, *J* 7 Hz, OCH_2Me), 4.04 (2 H, q, *J* 7 Hz, OCH_2Me), 2.26 (3 H, s, COMe), 1.32 (3 H, t, *J* 7 Hz, OCH_2Me), and 1.14 (3 H, t, *J* 7 Hz, OCH_2Me). This compound isomerized slowly to (**22**), and with hydrochloric acid (3M) in chloroform was hydrolysed to (**21**).

Reduction of the Ketone (**22**).—With sodium borohydride in 90% ethanol or $LiAlH(OBu^t)_3$ in THF, the product was ethyl 2-phenylthiobutanoate (**26**). With zinc borohydride[9] in dry ether (10 equiv., 4 h at room temperature under nitrogen), the product was *ethyl 2-ethyl-3-hydroxy-2-phenylthiobutanoate* (**24**) (96%), a mixture of diastereoisomers, R_F (A) 0.31, $\nu_{max.}$(film) 3 510 (OH), 1 724, and 1 703 cm^{-1} (C=O); δ($CDCl_3$) 7.2—7.6 (5 H, m, Ph), 3.9—4.3 (3 H, m, CHOH and CO_2CH_2Me), 3.06 (1 H, s, OH), 1.5—2.0 (2 H, m, SCH^*_2Me), and 0.8—1.4 (9 H, 13 lines, Me); *m/z* 268 (M^+, 3.5%), 224 (100), 178 (66), 151 (90), and 110 (52) (Found: C, 63.0; H, 7.5; S, 11.7. $C_{14}H_{20}O_3S$ requires C, 62.7; H, 7.5; S, 12.0%).

Reaction of the Alcohol (**24**) *with Acid.*—The alcohol with toluene-*p*-sulphonic acid (1 equiv.) in dry toluene (at reflux for 1.5 h), excess of P_2O_5 in dry benzene (reflux for 25 min), or toluene-*p*-sulphonic acid (2 equiv.) in benzene (reflux for 3 h) gave (**26**) and diphenyl disulphide as the main products.

Ethyl 3-Chloro-2-ethyl-2-phenylthiobutanoate (**27**) *and Ethyl 2-Chloro-2-ethyl-3-phenylthiobutanoate* (**28**).—The alcohol (**24**) (47 mg), a few drops of $SOCl_2$, and dry pyridine were kept in carbon tetrachloride (5 ml) at 0 °C for 5 min; hydrochloric acid (3M) was added, the CCl_4 layer was separated, and the aqueous layer was extracted with chloroform (2 × 5 ml). The extracts were dried (Na_2SO_4) and evaporated and preparative t.l.c. of the residue gave a 1:1 mixture of (**27**) and (**28**) (30 mg, 60%). The alcohol (**24**) (101 mg) with methanesulphonyl chloride (47 mg) and triethylamine (0.2 ml) in carbon tetrachloride (4 ml) gave after 6 d at room temperature and work-up as above, a 1:5 mixture of (**27**) and (**28**) (49 mg, 45%). This mixture did not react with DBN in CCl_4 or THF or sodium ethoxide in ethanol.

3,5-*Dimethyl-3-phenylthiohex-5-en-2-one* (**31**).—Under nitrogen, to petroleum-washed sodium hydride (0.17 g) in dry THF (30 ml) was added 3-phenylthiobutan-2-one (**30**) (0.95 g), followed after 0.5 h by methylallyl chloride (0.6 ml). The mixture was heated under reflux for 20 h, after which aqueous ammonium chloride was added, the THF layer separated, and the aqueous layer extracted with chloroform (3 × 20 ml). The extracts were dried (Na_2SO_4), evaporated, and the residue subjected to preparative t.l.c. to give the homoallyl ketone (0.81 g, 66%), R_F (A) 0.45, $\nu_{max.}$(film) 1 700 (C=O), 1 641 (C=C), and 896 cm^{-1} (C=CH_2); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 4.85 (1 H, s, C=CH_2*), 4.70 (1 H, s, C=CH_2*), 2.76 and 2.42 (2 H, ABq, J_{AB} 15 Hz, $CH^*_2C=CH_2$), 2.38 (3 H, s, COMe), 1.68 (3 H, s, C=CMe), and 1.36 (3 H, s, SCMe); *m/z* 234 (M^+, 8%), 191 (100), 149 (17), and 81 (40). The *semicarbazone* had m.p. 145—146 °C (from methanol–water) (Found: C, 61.5; H, 7.5; N, 14.2; S, 10.8. $C_{15}H_{21}N_3OS$ requires C, 61.8; H, 7.3; N, 14.4; S, 11.0%). Repetition of the above reaction with methylallyl iodide instead of the chloride (complete in 3.5 h at room temperature) gave 95% of (**31**).

3,5-*Dimethyl-3-phenylthiohex-5-en-2-ol* (**32**).—The ketone (**31**) (1.10 g) and sodium borohydride (60 mg) were stirred in 90% ethanol (20 ml) for 5 h, after which aqueous ammonium chloride was added and the mixture extracted with chloroform (3 × 15 ml). The extracts were dried (Na_2SO_4), evaporated, and subjected to preparative t.l.c. to give the *alcohol* (1.00 g, 91%), a mixture of diastereoisomers X and Y (4:5), R_F (A) 0.39 and 0.37, $\nu_{max.}$(film) 3 470 (OH), 1 638 (C=C), and 892 cm^{-1} (C=CH_2); δ($CDCl_3$) 7.2—7.6 (5 H, m, Ph), 4.96 (1 H, narrow m, C=CH_2), 4.87 (1 H, narrow m, C=CH_2), 3.68^X and 3.56^Y (1 H, each q, *J* 6 Hz, MeCHOH), 2.40 (1 H, s, OH), 2.44 and 2.14 (2 H, ABq, J_{AB} 14 Hz, $CH^*_2C=C$), 1.95 and 1.91 (3 H, each s, MeC=C), 1.27^Y and 1.15^X (3 H, each d, *J* 6 Hz, MeCHOH), and 1.21^Y and 1.17^X (3 H, each s, MeCS); *m/z* 236 (M^+, 14%), 191 (67), 181 (23), 110 (100), and 81 (26) (Found: C, 71.2; H, 8.6; S, 13.3. $C_{14}H_{20}OS$ requires C, 71.1; H, 8.5; S, 13.6%).

Dehydration of the Alcohol (**32**).—The alcohol (50 mg) and toluene (4 ml) were heated under reflux in a foil-wrapped flask and an excess of phosphorus pentaoxide was added. After 5 min, aqueous sodium hydrogen carbonate was added and the mixture extracted with chloroform (3 × 10 ml). The extracts were dried (Na_2SO_4), evaporated, and subjected to preparative t.l.c. to give 4-methyl-2-(1-phenylthioethyl)penta-1,4-diene (**34**)

(33 mg, 72%), R_F (A) 0.71, $\nu_{max.}$(film) 1 645, 1 635 (C=C), and 895 cm^{-1} (C=CH_2); δ($CDCl_3$) 7.2—7.5 (5 H, m, Ph), 4.92 (1 H, s, C=CH^*_2), 4.85 (2 H, s, C=CH^*_2), 4.77 (1 H, s, C=CH_2), 3.76 (1 H, q, *J* 7 Hz, SC*H*Me), 3.02 and 2.86 (2 H, ABq, J_{AB} 15 Hz, CH_2=CCH^*_2C=CH_2), 1.66 (3 H, s, *Me*C=CH_2), and 1.41 (3 H, d, *J* 7 Hz, *Me*CHS); *m/z* 218 (M^+, 24%), 149 (32), 110 (100), 108 (66), 93 (80), and 67 (51). This compound was also formed, but in lower yield and contaminated with other unidentifiable products, by the reaction of (**32**) with toluene-p-sulphonic acid in benzene or acetonitrile.

5-Chloro-3-methyl-3-phenylthiohex-5-en-2-one (**37**).—3-Phenylthiobutan-2-one (0.54 g, 3 mmol) in dry THF (3 ml) was added dropwise to a stirred, cooled (0 °C) solution of potassium t-butoxide (0.37 g, 3 mmol) in dry THF (20 ml) under a nitrogen atmosphere. After 0.5 h, a suspension of potassium iodide (0.5 g) in THF (4 ml) containing DMF (1 ml) and 2,3-dichloropropene (0.35 g, 3.3 mmol) was added, and the mixture stirred for 2 h at room temperature. The solution was diluted with water (100 ml) and extracted with dichloromethane (4 × 50 ml). The organic extracts were washed with brine (2 × 40 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure to give an oil. The product was isolated by column chromatography, eluting with ether–light petroleum (b.p. 40—60 °C), to give the ketone as an oil (0.59 g, 67%), R_F (B) 0.45, $\nu_{max.}$(film) 1 700 (C=O) and 1 630 cm^{-1} (C=C); δ($CDCl_3$) 7.3 (5 H, br s, PhS), 5.19 and 5.29 (2 H, each d, *J* 0.5 Hz, C=CH_2), 2.73 and 3.12 (2 H, ABq, *J* 15 Hz, CH^*_2CCl), 2.41 (3 H, s, MeCO), and 1.48 (3 H, s, PhSC*Me*).

5-Chloro-3-ethyl-3-phenylthiohex-5-en-2-one.—In the same way, 3-phenylthiopentan-2-one (0.39 g) and 2,3-dichloropropene (0.24 g) gave the *ketone* as a yellow oil (0.37 g, 71%), R_F (B) 0.48, $\nu_{max.}$(film) 1 700 (C=O) and 1 630 cm^{-1} (C=C); δ($CDCl_3$) 7.3 (5 H, br s, PhS), 5.23 and 5.33 (2 H, each d, *J* 1.5 Hz, C=CH_2), 2.78 and 2.98 (2 H, ABq, *J* 16 Hz, CH_2CCl), 2.43 (3 H, s, MeCO), 1.88 (2 H, br q, *J* 7 Hz, CH_2Me), and 1.06 (3 H, br t, *J* 7 Hz, CH_2*Me*).

5-Chloro-3-methyl-3-phenylthiohex-5-en-2-ol (**38**).—Sodium borohydride (25 mg, 0.75 mmol) was added to a vigorously stirred solution of the ketone (**37**) (0.55 g, 2.2 mmol) in ethanol (4.5 ml) and water (0.5 ml). After 4 h the solution was acidified (NH_4Cl) and extracted with dichloromethane (3 × 30 ml). The extracts were washed with water (2 × 20 ml), aqueous sodium hydrogen carbonate (2 × 20 ml), and brine (2 × 15 ml), and then dried ($MgSO_4$). Solvent removal under reduced pressure gave the alcohol (a mixture of diastereoisomers X and Y) (0.55 g, 100%) as an oil, R_F (B) 0.25 and 0.20, $\nu_{max.}$(film) 3 600—3 200 (OH) and 1 630 cm^{-1} (C=C); δ($CDCl_3$) 7.2—7.6 (5 H, m, PhS), 5.32 and 5.30 (X and Y) (each 1 H, d, 0.5 Hz, C=CH_2), 3.82 (X) and 3.63 (Y), (1 H, q, *J* 6.5 Hz, MeC*H*OH), 2.88 and 2.45 (X and Y) (2 H, ABq, *J* 15 Hz, CH_2CCl), 1.32 (X) and 1.18 (Y) (3 H, d, *J* 6.5 Hz, *Me*CHOH), and 1.29 (X and Y) (3 H, s, PhSCMe).

2-Chloro-4-(1-phenylthioethyl)penta-1,4-diene (**39**).—The alcohol (**38**) (0.255 g, 1 mmol) and toluene-*p*-sulphonic acid (0.19 g, 1 mmol) were heated under reflux in dry benzene (5 ml) for 30 min in the dark. The mixture was cooled, poured onto ice and 1M-aqueous sodium hydroxide, and extracted with dichloromethane (3 × 25 ml). The extracts were washed with brine (2 × 15 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure and p.l.c. (all in the dark) gave the diene (0.21 g, 88%), as an oil, R_F (B) 0.8, $\nu_{max.}$(film) 1 630 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.5 (5 H, m, PhS), 5.18—5.26 (2 H, m, ClC=CH_2), 4.96 (2 H, s, C=CH_2), 3.74 (1 H, q, *J* 7 Hz, PhSC*H*Me), 3.19 and 3.29 (2 H, ABq, *J* 16 Hz, CH^*_2CCl), and 1.42 (3 H, d, *J* 7 Hz, PhSCH*Me*). Rearrangement of the same alcohol with P_2O_5 in benzene gave the same diene (74%)

Alkylation of Phenylthioacetone with Prenyl Bromide.—Under nitrogen, phenylthioacetone (0.92 g) was added to petroleum-washed sodium hydride (0.14 g) in dry THF (30 ml), followed after 0.5 h by prenyl bromide (0.84 g). The mixture was stirred overnight and worked up as for (**31**) above. Preparative t.l.c. gave phenylthioacetone (0.23 g), phenyl prenyl sulphide (0.18 g) and 0.50 g (39%, 53% based on recovered phenylthioacetone) of an 8:1 mixture of (**41**) and (**40**), R_F (A) 0.55. 6-Methyl-3-phenylthiohept-5-en-2-one (**41**) had $\nu_{max.}$(film) 1 710 (C=O) and 1 671 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 5.14 (1 H, t, *J* 7 Hz, CH_2C*H*=C), 3.64 (1 H, t, *J* 7.5 Hz, SC*H*CH_2), 2.3—2.6 (2 H, m, CHCH_2CH=C), 2.22 (3 H, s, COMe), and 1.71 and 1.62 (each 3 H, s, C=CMe_2). 4,4-Dimethyl-3-phenylthiohex-5-en-2-one (**40**) had $\nu_{max.}$(film) 1 710 (C=O) and 1 637 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 6.04 (1 H, dd, *J* 10, 18 Hz, C*H*=CH_2), 5.0—5.2 (2 H, m, C=CH_2), 3.62 (1 H, s, SCH), 2.14 (3 H, s, COMe), and 1.25* and 1.30* (each 3 H, s, CMe_2). The mixture had *m/z* 234 (M^+, 14%), 193 (28), 166 (51), 125 (100), 123 (43), and 81 (95) (Found: M^+, 234.1075. $C_{14}H_{18}OS$ requires *M*, 234.1078).

6-Methyl-3-phenylthiohept-5-en-2-ol (**42**).—The above mixture of ketones (0.40 g) was reduced by sodium borohydride to give, after preparative t.l.c., (**42**) (0.30 g, 74%), R_F (A) 0.42; $\nu_{max.}$(film) 3 410 (OH) and 1 670 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.6 (5 H, m, Ph), 5.18 (1 H, t, *J* 7 Hz, CH_2C*H*=C), 3.82 [1 H, quint, *J* 6 Hz, MeC*H*(OH)CH], 3.02 (1 H, dt, *J* 8 and 6 Hz, CHC*H*CH^*_2), 2.0—2.6 (3 H, m, CHCH^*_2CH=C and OH), 1.62 and 1.72 (each 3 H, s, C=CMe_2), and 1.29 (3 H, d, *J* 6 Hz, *Me*CHOH); *m/z* 236 (M^+, 49%), 191 (14), 167 (100), 149 (64), 110 (30), and 81 (77) (Found: C, 71.2; H, 8.7; S, 13.4. $C_{14}H_{20}OS$ requires C, 71.1; H, 8.5; S, 13.6%); and *4,4-dimethyl-3-phenylthiohex-5-en-2-ol* (0.05 g, 12%), R_F (A) 0.46, $\nu_{max.}$(film) 3 440 (OH), 1 633 (C=C), and 912 cm^{-1} (C=CH_2); δ($CDCl_3$) 7.1—7.6 (5 H, m, Ph), 6.01 (1 H, dd, *J* 10.5, 17.5 Hz, C*H*=CH_2), 5.07 (1 H, d, *J* 17.5 Hz, *E* CH=CH_2), 5.05 (1 H, d, 10.5 Hz, *Z* CH=CH_2), 4.1—4.4 [1 H, m, MeC*H*(OH)CH], 2.91 (1 H, d, *J* 1.5 Hz, SC*H*CHOH), 1.69 (1 H, br d, *J* 6 Hz, CHO*H*), and 1.24* and 1.23* (each 3 H, s, CMe_2); *m/z* 236 (M^+, 23%), 191 (11), 167 (100), 149 (80), 110 (61), 109 (32), and 81 (29) (Found: M^+, 236.1236. $C_{14}H_{20}OS$ requires *M*, 236.1234). Reaction of (**42**) with toluene-*p*-sulphonic acid or P_2O_5 in toluene at reflux gave no identifiable products.

Alkylation of 3-Phenylthiobutan-2-one (**30**) *with Prop-2-ynyl Halides.*—(a) *Prop-2-ynyl chloride.* Under nitrogen, 3-phenylthiobutanone (2.35 g) was added to petroleum-washed sodium hydride (0.41 g) in dry THF (50 ml), followed after 0.5 h by prop-2-ynyl chloride (1.0 ml). The mixture was heated under reflux for 6 h and worked up as for (**31**) above. The resulting oil was passed down a column of silica with dichloromethane–carbon tetrachloride (1:1) as eluant to give a 2:1 mixture (1.72 g, 89%) of (**43**) and (**44**), R_F (A) 0.55. Phenylthiopropadiene[23] (**43**) had δ($CDCl_3$) 7.0—7.5 (5 H, m, Ph), 5.92 (1 H, t, *J* 6 Hz, SC*H*=C=CH_2), and 4.92 (2 H, d, *J* 6 Hz, SCH=C=CH_2), 1 phenylthiopropyne[23] (**44**) had δ($CDCl_3$) 7.0—7.5 (5 H, m, Ph), and 2.04 (3 H, s, C≡CMe). The mixture had *m/z* 148 (M^+, 100%), 147 (69), 135 (25), 110 (100), 109 (83), 77 (36), and 51 (33).

(b) *Prop-2-ynyl iodide.* Repetition of the above reaction with prop-2-ynyl iodide (room temperature, 3 d) gave (**43**) and (**44**) (39%) and *3-methyl-3-phenylthiohex-5-yn-2-one* (**45**) (60%), R_F (A) 0.34, $\nu_{max.}$(film) 3 290 (C≡C–H), 2 125 (C≡C), and 1 700 cm^{-1} (C=O); δ($CDCl_3$) 7.2—7.5 (5 H, m, Ph), 2.50 and 2.56 (2 H, ABX system, J_{AB} 20, J_{AX} = J_{BX} 3 Hz, CH^*_2C≡CH), 2.40 (3 H, s, COMe), 2.1 (1 H, m, C≡CH), and 1.56 (3 H, s, COMe); *m/z* 218

(M^+, 10%), 175 (78), 110 (35), 69 (55), and 43 (100) (Found: M^+, 218.0766. $C_{13}H_{14}OS$ requires M, 218.0765).

3-*Methyl*-3-*phenylthiohex*-5-*yn*-2-*ol* (**46**).—Reduction of the foregoing ketone (1.60 g) with sodium borohydride (0.10 g) in 90% ethanol (30 ml) gave the *alcohol* (1.61 g, 99%), a mixture of diastereoisomers X and Y (3:1), R_F (A) 0.30, $\nu_{max.}$(film) 3 460 (OH), 3 300 (C≡C–H), and 2 125 cm^{-1} (C≡C), δ($CDCl_3$) 7.5—7.7 (2 H, m, ArH *o* to S), 7.2—7.4 (3 H, m, Ar), 3.82 (Y) and 3.72 (X) (1 H, each q, *J* 6 Hz, MeC*H*OH), 2.84 (1 H, br s, OH), 2.1—2.6 (3 H, m, CH_2C≡CH), 1.29 (3 H, s, MeCS), and 1.23 (X) and 1.29 (Y) (3 H, each d, *J* 6 Hz, *Me*CH); *m/z* 220 (M^+, 22%), 176 (21), 175 (94), 110 (100), and 109 (**31**) (Found: C, 71.1; H, 7.5; S, 14.3. $C_{13}H_{16}OS$ requires C, 70.9; H, 7.3; S, 14.5%).

Attempted Hydrolysis of the Acetylenic Alcohol (**46**).—The alcohol was decomposed by trifluoracetic acid, and by red mercury(II) oxide, trichloroacetic acid, and boron trifluoride–diethyl ether in methanol.[24] With formic acid, or mercury(II) sulphate in 85% formic acid[25] it gave only the corresponding formic ester and recovered starting material. The formate had R_F (A) 0.27, δ($CDCl_3$) (partial spectrum only) 7.99 (1 H, s, OCHO) and 5.27 (1 H, q, *J* 6.5 Hz, MeC*H*).

4-*Methyl*-5-*phenylthiohex*-3-*en*-1-*yne* (**48**).—The alcohol (**46**) (56 mg) and dry benzene (4 ml) were heated under reflux and an excess of P_2O_5 was added. Heating was continued for 5 min after which the mixture was worked up as for (**34**) above. Preparative t.l.c. gave the *enyne* (39 mg, 76%), R_F (A) 0.60, $\nu_{max.}$(film) 3 300 (C≡C–H), 2 100 (C≡C), and 1 618 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 5.14 (1 H, s, C=CH), 3.75 (1 H, q, *J* 7 Hz, MeC*H*S), 3.00 (1 H, d, *J* 2 Hz, C=CHC≡C*H*), 2.01 (3 H, d, *J* 1 Hz, *Me*C=CH), and 1.41 (3 H, d, *J* 7 Hz, *Me*CHS); *m/z* 202 (M^+ 5%), 110 (54), 83 (100), 77 (42), and 55 (54) (Found: M^+, 202.0815. $C_{13}H_{14}S$ requires M, 202.0815). Toluene as solvent gave the same result.

4-*Methyl*-5-*phenylthiohex*-3-*en*-2-*one* (**49**).—The alcohol (**46**) (61 mg), benzene (4 ml), water (1 drop), and toluene-*p*-sulphonic acid (60 mg) were heated under reflux for 20 min. Work-up as for (**34**) above and preparative t.l.c. gave the vinyl ketone (35 mg, 57%), a mixture of *E* and *Z* isomers (4:1), R_F (A) 0.38, $\nu_{max.}$(film) 1 682 (C=O) and 1 613 cm^{-1} (C=C); δ($CDCl_3$) 7.2—7.5 (5 H, m, Ph), 5.96 (*Z*) and 5.74 (*E*) (1 H, each s, C=CHCO), 3.69 (1 H, q, *J* 7 Hz, MeC*H*S), 2.19 and 1.93 (3 H, each d, *J* 1 Hz, *Me*C=CH), 1.99 (*E*) and 1.94 (*Z*) (3 H, each s, COMe), and 1.44 (*E*) and 1.42 (*Z*) (3 H, each d, *J* 7 Hz, *Me*CHS); *m/z* 220 (M^+, 67%), 177 (29), 111 (71), 110 (80), 83 (10), and 55 (50) (Found: M^+, 220.0921. $C_{13}H_{16}OS$ requires M, 220.0921).

3-*Methyl*-3-*phenylthio*-*oct*-5-*yn*-2-*one* (**51**).—3-Phenylthiobutan-2-one (0.72 g, 4 mmol) in dry THF (5 ml) was added dropwise to a stirred, cooled (0 °C) solution of potassium t-butoxide (0.45 g, 4 mmol) in dry THF (20 ml) under a nitrogen atmosphere. After 0.5 h, a suspension of potassium iodide (0.1 g) in THF (4 ml) containing DMF (1 ml) and 1-bromopent-2-yne[13] was added, and the mixture stirred for 2 h at room temperature. The solution was diluted with water (100 ml) and extracted with dichloromethane (4 × 50 ml). The organic extracts were washed with brine (2 × 40 ml), dried ($MgSO_4$), and the solvent was evaporated under reduced pressure to give an oil. The product was isolated by column chromatography, eluting with ether–light petroleum (b.p. 40—60 °C), to give the *ketone* as a colourless oil (0.833 g, 85%), R_F (B) 0.40, $\nu_{max.}$(film) 1 695 (C=O); δ($CDCl_3$) 7.2—7.5 (5 H, m, PhS), 2.0—2.6 (4 H, m, CH_2C≡CCH_2), 2.38 (3 H, s, COMe), 1.18 (3 H, s, PhSC*Me*), and 1.11 (3 H, t, *J* 7 Hz, CH_2Me) (Found: M^+, 246.1079. $C_{15}H_{18}OS$ requires M, 246.1079), *m/z* 246 (15%), 203 (100, M – COMe), and 110 (48, $PhSH^+$).

3-*Methyl*-3-*phenylthio*-*oct*-5-*yn*-2-*ol* (**52**).—Sodium borohydride (42 mg, 1 mmol) was added to a vigorously stirred solution of the above ketone (**51**) (0.9 g, 3.7 mmol) in ethanol (9 ml) containing water (1 ml). After 3 h the solution was poured onto crushed ice–aqueous ammonium chloride (100 ml) and extracted with dichloromethane (3 × 30 ml). The organic extracts were washed with water (2 × 20 ml), aqueous sodium hydrogen carbonate (2 × 20 ml), and brine (2 × 15 ml), and then dried ($MgSO_4$). Solvent removal under reduced pressure gave the *alcohol*, as a mixture of diastereoisomers (X and Y) (0.9 g, 100%), as an oil, R_F (B) 0.25 and 0.20, $\nu_{max.}$(film) 3 200—3 000 (OH); δ($CDCl_3$) 7.2—7.7 (5 H, m, PhS), 3.71 (X) and 3.82 (Y), (1 H, q, *J* 6.5 Hz, CHO), 2.0—2.6 (4 H, m, CH_2C≡CCH_2), 1.24 (3 H, s, PhSCMe), 1.0—1.3 (6 H, m, 2 × Me) (Found: M^+, 248.1235. $C_{15}H_{20}OS$ requires M, 248.1229), *m/z* 248 (30%), 203 (65, M – MeCHOH), 181 (40, M – EtC≡CCH_2), and 110 (100, $PhSH^+$).

6-*Methyl*-7-*phenylthio*-*oct*-5-*en*-3-*yne* (**53**).—The above alcohol (**52**) (0.76 g, 3 mmol) and phosphorus pentaoxide (1 g) in benzene (18 ml) were heated under reflux under a nitrogen atmosphere for 2 h. The cooled suspension was poured carefully into crushed ice–1M-aqueous sodium hydroxide and extracted with dichloromethane (3 × 25 ml). The organic extracts were washed with brine (2 × 15 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure. The product was purified by p.l.c. to give the *enyne* as an oil (0.57 g, 80%) as a mixture of geometrical isomers (X and Y, 1:9), R_F (B) 0.60, δ($CDCl_3$) 7.1—7.5 (5 H, m, PhS), 5.24—5.26 (1 H, m, C=CH), 3.87 (X) and 3.76 (Y) (1 H, q, *J* 7 Hz, PhSC*H*Me), 2.32 (2 H, dq, *J* 2.5 and 7 Hz, C≡CCH_2Me), 1.97 (Y) (3 H, s, C=CMe), 1.82 (X) (3 H, dd, *J* 4.5 and 0.5 Hz, C=CMe), 1.43 (X) and 1.38 (Y) (3 H, d, *J* 7 Hz, PhSCH*Me*), and 1.14 (3 H, t, *J* 7 Hz, CH_2*Me*) (Found: M^+, 230.1097. $C_{15}H_{18}S$ requires M, 230.1113), *m/z* 230 (28%), 215 (10, M – Me), 121 (100, M – PhS), and 110 (30, PhSH). This product was isolated from the rearrangement of the alcohol using toluene-*p*-sulphonic acid monohydrate in benzene.

Attempted Hydrolysis of the Enyne (**53**).—The addition of water (1.1 equiv.) to the toluene-*p*-sulphonic acid reaction failed to hydrolyse the enyne. After prolonged heating there was considerable decomposition. The enyne was rapidly decomposed by trifluoroacetic acid, 80% aqueous sulphuric acid, red mercuric oxide and boron trifluoride–diethyl etherate in methanol, and mercuric sulphate in acetic acid.

Attempted Hydrolysis of the Alcohol (**38**) *and the Diene* (**39**).—Both these compounds were rapidly decomposed by trifluoroacetic acid, 95% aqueous sulphuric acid,[11] and polyphosphoric acid at 100 °C. Slow decomposition resulted from the addition of 1.1 equivalent of water to the toluene-*p*-sulphonic acid reaction after prolonged heating.

5-*Phenyl*-5,5-*bis*(*phenylthio*)*pentan*-2-*one* (**56**).—Butyl-lithium (6.5 ml, 1.55M in hexane, 10 mmol) was added to a stirred, cooled (−78 °C) solution of 1-phenyl-1,1-bis(phenylthio)-methane (3.1 g, 10 mmol) in dry THF (60 ml), under a nitrogen atmosphere. After 1 h copper(I) iodide (0.95 g, 5 mmol) was added and the solution again left for 1 h at −78 °C before methyl vinyl ketone (0.35 g, 5 mmol) in THF (10 ml) was slowly added. After a further 2 h at −78 °C the reaction was quenched with water (50 ml) and extracted into ether (3 × 30 ml). The organic extracts were filtered through Hyflo, washed with brine (2 × 20 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure to give the ketone (1.7 g, 89%) as prisms, m.p.

77.5—78.5 °C [from light petroleum (b.p. 30—40 °C)–ether], this compound has been reported[25] without experimental details, R_F (B) 0.21 (Found: C, 72.8; H, 6.10; S, 16.6%. Calc. for $C_{23}H_{22}OS_2$: C, 73.0; H, 5.85; S, 16.90%). The same product was also prepared from the lithium salt of 1-phenyl-1,1-bis(phenylthio)methane in 83% yield.

Attempted Oxidation of the Adduct (**56**).—The adduct, when treated with MCPBA (1 equiv.) in either ether at 0 °C, or dichloromethane at −78 °C, or with sodium metaperiodate (1 equiv.) in methanol–water (2:1) at room temperature, gave predominantly 1-phenylpentane-1,4-dione,[25] as an oil R_F (C) 0.25, $\nu_{max.}$(film) 1 720 (MeCO) and 1 690 (PhCO).

2-*Methyl*-1-*phenylsulphinyl*-1-*phenylthiopropane*.—*m*-Chloroperbenzoic acid (1.9 g, 11 mmol) in ether (22 ml) was added dropwise to a stirred, cooled (0 °C) solution of 2-methyl-1,1-bis(phenylthio)propane[5] (2.74 g, 10 mmol) in ether (40 ml), under a nitrogen atmosphere. After 15 min the solution was poured into aqueous sodium hydrogen carbonate (90 ml) and the organic layer separated. The aqueous layer was washed with ether (2 × 30 ml), and the combined organic extracts were washed with aqueous sodium hydrogen carbonate (2 × 25 ml) and brine (2 × 30 ml) and dried ($MgSO_4$). Solvent removal under reduced pressure gave a yellow oil, which turned into a waxy solid with time. This was recrystallised from pentane–ether at −10 °C (with some decomposition occurring when the solution was warmed above 30 °C) to give the sulphoxide as one diastereoisomer (1.61 g, 58%) as needles, m.p. 72—73 °C (decomp.), shown by t.l.c., n.m.r., and mass spectra to contain *ca.* 15% of an impurity (M + 16). The sulphoxide had R_F (ether) 0.60, δ($CDCl_3$) 6.7—7.7 (10 H, m, PhS and PhSO), 3.93 (1 H, d, J 2.5 Hz, C*H*CHMe$_2$), 2.96 (1 H, d sept, J 2.5 and 6.5 Hz, CHC*H*Me$_2$), and 1.20 and 1.11 (2 × 3 H, each d, J 6.5 Hz, CH*Me*$_2$); *m/z* 165 (100%, M − PhSO), 164 (50, M − PhSOH), and 110 (95, PhSH$^+$). This product was also obtained in 15% yield by oxidation using sodium periodate in methanol–water (2:1).

4-*Oxo*-3-*phenylthiopentanenitrile* (**58**).—Under nitrogen, phenylthioacetone (1.56 g) was added to petroleum-washed sodium hydride (0.23 g) in dry THF (25 ml), followed after 0.5 h by iodoacetonitrile (1.57 g). The mixture was stirred for 3 days, ammonium chloride and sodium thiosulphate solutions were added and the THF layer separated; the aqueous layer was then extracted with chloroform (3 × 15 ml). The combined organic fractions were dried (Na_2SO_4) and evaporated to give a brown oil, which was passed down a column of silica with dichloromethane as eluant to give phenylthioacetone (0.39 g), phenylthioacetonitrile (0.41 g, 29%, 39% based on recovered starting material), and the nitrile (**58**) (0.61 g, 33%, 44% based on recovered starting material), R_F (A) 0.24, $\nu_{max.}$(film) 2 260 (CN) and 1 710 cm^{-1} (C=O); δ($CDCl_3$) 7.2—7.5 (5 H, m, Ph), 3.84 (1 H, dd, J 6.5, 8 Hz, SC*H*CH$_2^*$CN), 2.61 and 2.69 (2 H, ABX system, J_{AB} 17, J_{BX} 6.5, J_{AX} 8 Hz, CHCH_2^*CN), and 2.43 (3 H, s, COMe); *m/z* 205 (M^+, 52%), 162 (100), 110 (34), and 109 (70). The *semicarbazone* had m.p. 132—133 °C (from methanol–water) (Found: C, 54.9; H, 5.4; N, 21.1; S, 12.0. $C_{12}H_{14}N_4OS$ requires C, 54.9; H, 5.4; N, 21.4; S, 12.2%).

4-*Hydroxy*-3-*phenylthiopentanenitrile* (**59**).—Under nitrogen, zinc borohydride[9] (9 ml of a 1M solution in ether, 5 equiv.) was added to the foregoing ketone (0.37 g) in dry ether (40 ml). Reaction was complete in less than 10 min by t.l.c. Ammonium chloride was added, the ether layer separated, and the aqueous layer extracted with ether (3 × 15 ml). The combined organic fractions were dried ($MgSO_4$) and evaporated to give the pure *hydroxy nitrile* (0.32 g, 86%), a single diastereoisomer, R_F (A) 0.21, $\nu_{max.}$(film) 3 440 (OH) and 2 255 cm^{-1} (CN); δ($CDCl_3$) 7.2—7.6 (5 H, m, Ph), 4.05 [1 H, dq, J 4.5, 6.5 Hz, MeC*H*(OH)CH], 3.23 (1 H, dt, J 4.5, 7 Hz, SCH), 2.67 and 2.77 (2 H, ABX system, J_{AB} 16, J_{AX} = J_{BX} 7 Hz, CHCH_2^*CN), 2.4 (1 H, br s, OH), and 1.27 (3 H, d, J 6.5 Hz, *Me*CHOH); *m/z* 207 (M^+, 16%), 163 (17), 136 (100), 135 (27), and 110 (21) (Found: C, 63.8; H, 6.5; N, 6.9; S, 15.2. $C_{11}H_{13}NOS$ requires C, 63.7; H, 6.3; N, 6.8; S, 15.5%). Sodium borohydride reduction of the ketone (**58**) also gave this alcohol (75% after preparative t.l.c.).

Butyl 4-*Phenylthiopent*-2-*enoate* (**65b**; R = Bu).—The lactone[19] (**63b**) (190 mg), toluene-*p*-sulphonic acid (175 mg, 1 equiv.), dry benzene (10 ml), and butanol (AnalaR; 0.1 ml) were heated under reflux for 48 h, after which aqueous sodium hydrogen carbonate was added; the benzene layer was then separated and the aqueous layer extracted with chloroform (3 × 10 ml). The combined organic fractions were dried (Na_2SO_4), evaporated, and subjected to preparative t.l.c. to give the *ester* (205 mg, 85%), *E*-isomer only, R_F (A) 0.54, $\nu_{max.}$(film) 1 715 (C=O) and 1 644 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 6.87 (1 H, dd, J 7, 15.5 Hz, CHC*H*=CHCO), 5.56 (1 H, dd, J 1, 15.5 Hz, CHCH=C*H*CO), 4.12 (2 H, t, J 6.5 Hz, $CO_2CH_2CH_2$), 3.79 (1 H, br quint, J 7—8 Hz, MeC*H*–CH=CH), 1.2—1.8 (4 H, m, $CH_2CH_2CH_2Me$), 1.44 (3 H, d, J 7 Hz, *Me*CHS), and 0.95 (3 H, t, J 7 Hz, *Me*CH$_2$); *m/z* 264 (M^+, 67%), 207 (14), 191 (21), 190 (23), 163 (54), 110 (86), and 99 (100) (Found: C, 67.9; H, 7.8; S, 12.3. $C_{15}H_{20}O_2S$ requires C, 68.1; H, 7.6; S, 12.1%). Stopping the reaction after 24 h gave a 4:5 mixture of (**65b**) and butyl 3-butoxy-4-phenylthiopentanoate (**72**), R_F (A) 0.60, n.m.r. spectrum shows the presence of two OBu groups. This compound was converted quantitatively into (**65b**; R=Bu) by heating with toluene-*p*-sulphonic acid in benzene for 24 h. Similarly prepared were *ethyl* 4-*phenylthiopent*-2-*enoate* (**65b**; R = Et) from (**63b**), toluene-*p*-sulphonic acid, ethanol, and benzene at reflux for 2 days in 88% yield after preparative t.l.c. [the n.m.r. spectrum before p.l.c. showed a 1:1 mixture of this compound and ethyl toluene-*p*-sulphonate: δ($CDCl_3$) 7.79 (2 H, d, J 7.5 Hz, ArH *o* to SO_2), 7.32 (2 H, d, J 8.5 Hz, ArH *m* to SO_2), 4.10 (2 H, q, J 7 Hz, SO_3CH_2Me), 2.44 (3 H, s, *Me*Ar), and 1.28 (3 H, t, J 7 Hz, *Me*CH$_2$)]; R_F (A) 0.49, $\nu_{max.}$(film) 1 712 (C=O) and 1 646 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 6.87 (1 H, dd, J 8, 15.5 Hz, CH–C*H*=CHCO), 5.56 (1 H, br quint, J 7—8 Hz, CH–CH=C*H*CO), 4.15 (3 H, d, J 7 Hz, CO_2CH_2Me), 3.78 (1 H, br quint, J 7—8 Hz, MeC*H*–CH=CH), 1.43 (3 H, d, J 7 Hz, *Me*CHS), and 1.25 (3 H, t, J 7 Hz, *Me*CH$_2$); *m/z* 236 (M^+, 39%), 191 (14), 163 (38), 127 (21), 110 (100), 109 (92), 99 (88), and 73 (88) (Found: C, 65.8; H, 6.9; S, 13.3. $C_{13}H_{16}O_2S$ requires C, 66.1; H, 6.8; S, 13.6%); and *butyl* 3-*methyl*-4-*phenylthiopent*-2-*enoate* (**65h**; R=Bu) from the lactone (**63h**) toluene-*p*-sulphonic acid, butanol, and toluene at reflux for 24 h in 75% yield after preparative t.l.c., a mixture of *E* and *Z* isomers (6:1), R_F (A) 0.57, $\nu_{max.}$(film) 1 710 (C=O) and 1 641 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 5.58 (*Z*), and 5.48 (*E*) (1 H, each s, C=CHCO), 4.05 (2 H, t, J 6.5 Hz, CO_2CH_2Me), 3.72 (1 H, q, J 7 Hz, MeC*H*S), 2.24 (*E*) and 1.93 (*Z*) [3 H, each d, J (*E*) 1 Hz, J (*Z*) 1.5 Hz, *Me*C=CH], 1.2—1.7 (4 H, m, CH_2), 1.42 (3 H, d, J 7 Hz, *Me*CHS), and 0.93 (3 H, t, J 6.5 Hz, *Me*CH$_2$); *m/z* 278 (M^+, 18%), 177 (14), 113 (100), and 110 (68) (Found: C, 69.3; H, 8.0; S, 11.8. $C_{16}H_{22}O_2S$ requires C, 69.0; H, 8.0; S, 11.5%).

Rearrangement of the Lactone (**63i**) *with Toluene*-p-*sulphonic Acid and an Alcohol*.—(a) *Ethanol*. The lactone (45 mg), toluene-*p*-sulphonic acid (32 mg, 1 equiv.), ethanol (2 drops), and dry benzene (4 ml) were heated under reflux for 3 d. Work-up as above and preparative t.l.c. gave a 4:1 mixture of (**65i**; R = Et) (itself a 5:1 mixture of *E* and *Z* isomers) and (**66i**; R = Et) (32 mg, 64%). *Ethyl* 3-*ethyl*-4-*phenylthiopent*-2-*enoate* (**65i**; R = Et) had R_F (A) 0.55, $\nu_{max.}$(film) 1 711 (C=O) and 1 636 cm^{-1} (C=C);

δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 5.58 (*Z*) and 5.54 (*E*) (1 H, each s, C=CHCO), 4.11 (2 H, q, *J* 7 Hz, CO_2CH_2Me), 3.74 (1 H, q, *J* 7 Hz, SC*H*Me), 2.2—2.8 (2 H, m, $MeCH_2^*C$=C), and 1.0—1.5 (9 H, m, Me). *Ethyl* 3-(1-*phenylthioethyl*)*pent*-3-*enoate* (**66i**; R=Et) had R_F (A) 0.55, $\nu_{max.}$(film) 1 728 cm^{-1} (C=O); δ($CDCl_3$) 7.1—7.5 (5 H, m, Ph), 5.40 (1 H, q, *J* 7 Hz, MeC*H*S), 3.23 (2 H, s, CH_2CO), 1.56 (3 H, d, *J* 7 Hz, *Me*CH=C), and 1.0—1.5 (6 H, m, Me). The mixture had *m*/*z* 264 (M^+, 36%), 219 (18), 155 (100), 127 (69), 110 (63), 109 (56), 83 (51), and 81 (69) (Found: M^+, 264.1174. $C_{15}H_{20}O_2S$ requires *M*, 264.1183).

(b) *Butanol.* The lactone (45 mg), toluene-*p*-sulphonic acid (32 mg, 1 equiv.), butanol (2 drops), and dry toluene (4 ml) were heated under reflux for 24 h. Direct preparative t.l.c. on the red solution remaining gave a 4:1 mixture of (**65i**; R = Bu) (itself a 5:1 mixture of *E* and *Z* isomers) and (**66i**; R = Bu) (31 mg, 49%). *Butyl* 3-*ethyl*-4-*phenylthiopent*-2-*enoate* (**65i**; R = Bu) had R_F (A) 0.59, $\nu_{max.}$(film) 1 713 (C=O) and 1 635 cm^{-1} (C=C); δ($CDCl_3$) 7.1—7.6 (5 H, m, Ph), 5.59 (*Z*) and 5.53 (*E*) (1 H, each s, C=CHCO), 4.18 (2 H, t, *J* 7 Hz, $CO_2CH_2CH_2$), 3.74 (1 H, q, *J* 7 Hz, MeC*H*S), 2.8—2.2 (2 H, m, C=CCH_2^*), and 1.8—0.8 (13 H, m, Pr and Me). *Butyl* 3-(1-*phenylthioethyl*)*pent*-3-*enoate* (**66i**; R = Bu) had R_F (A) 0.59; $\nu_{max.}$(film) 1 730 cm^{-1} (C=O); δ($CDCl_3$) 7.6—7.1 (5 H, m, Ph), 5.41 (1 H, q, *J* 6.5 Hz, MeC*H*=C), 4.08 (2 H, t, *J* 7 Hz, $CO_2CH_2CH_2$), 3.74 (1 H, q, *J* 7 Hz, MeC*H*S), 3.25 (2 H, s, CH_2CO), 1.57 (3 H, d, *J* 6.5 Hz, *Me*CH=C), and 0.8—1.8 (10 H, m, Pr and Me). The mixture had *m*/*z* 292 (M^+, 18%), 236 (23), 167 (41), 149 (29), 127 (100), and 110 (64) (Found: C, 69.9; H, 8.1; S, 11.3. $C_{17}H_{24}O_2S$ requires C, 69.8; H, 8.3; S, 11.0%).

Rearrangement of the Lactone (**63e**) *with Toluene*-p-*sulphonic Acid and Butanol.*—The lactone (0.13 g), toluene-*p*-sulphonic acid (0.12 g, 1 equiv.), butanol (AnalaR; 0.1 ml), and dry toluene (5 ml) were heated under reflux for 24 h. The mixture was worked up as above. Preparative t.l.c. gave a mixture of (**65e**; R = Bu) and (**66e**; R = Bu) (0.13 g, 80%), R_F (A) 0.63. The mixture was unchanged after a further 2 d under the same conditions. It was added to a solution of sodium butoxide (from butanol and petroleum-washed sodium hydride) in butanol (20 ml), stirred for 20 h at room temperature and heated under reflux for 1 h. Aqueous ammonium chloride was added, the butanol layer separated, and the aqueous layer extracted with chloroform (3 × 10 ml). The combined organic fractions were dried (Na_2SO_4) and evaporated to give a 1:1 mixture of (**65e**; R = H) (itself a 1:1 mixture of geometric isomers) and (**67e**; R = H) (4:3 mixture of geometric isomers A and B). 3-*Ethyl*-4-*phenylthiobut*-2-*enoic acid* (**65e**; R = H) had R_F (Et_2O–1% AcOH) 0.90, δ($CDCl_3$) 9.8 (1 H, br s, CO_2H), 7.1—7.5 (5 H, m, Ph), 6.02—6.08 (1 H, each s, C=CHCO), 3.69 and 3.63 (2 H, each s, SCH_2), 2.1—2.5 (2 H, m, $MeCH_2C$=C), and 1.11 and 1.04 (3 H, each t, *J* 7.5 Hz, *Me*CH_2). 3-(*Phenylthiomethyl*)*pent*-3-*enoic acid* (**66e**; R = H) had R_F (Et_2O–1% AcOH) 0.90, δ($CDCl_3$) 9.8 (1 H, br s, CO_2H), 7.1—7.5 (5 H, m, Ph), 5.51 (1 H, q, *J* 7 Hz, MeC*H*=C), 3.41 (A), 3.29 (A), 3.32 (B) and 3.19 (B) (4 H, each s, CH_2), and 1.59 (A) and 1.46 (B) (3 H, each d, *Me*CH=C). The mixture had $\nu_{max.}$(film) 1 707 cm^{-1} (C=O); *m*/*z* 222 (M^+67%), 113 (17), 110 (100), and 71 (30) (Found: M^+, 222.0702. $C_{12}H_{14}O_2S$ requires *M*, 222.0714).

Reaction of the Lactones (**73**) *and* (**74**) *with Toluene*-p-*sulphonic Acid and an Alcohol.*—With butanol and toluene-*p*-sulphonic acid in toluene at reflux for 3 d, (**73**) gave diphenyl disulphide as the main phenylthio-containing product; with ethanol and toluene-*p*-sulphonic acid in benzene at reflux for 2 d, (**74**) gave an unidentified mixture of products.

Methyl Phenyl(*phenylthio*)*acetate.*—Potassium hydroxide (11.8 g, 0.21 mol) in methanol (50 ml) was added dropwise to a stirred solution of thiophenol (11.5 g, 0.1 mol) and 2-bromo-2-phenylthioacetic acid (21.5 g, 0.1 mol) in dry ethanol (150 ml) at 0 °C under nitrogen. After 24 h at room temperature, the mixture was acidified with conc. H_2SO_4 (10 g) in methanol (100 ml) and left at room temperature for 3 days. The solvents were evaporated under reduced pressure and the mixture was diluted with water (250 ml) and extracted with dichloromethane (4 × 100 ml). The extracts were washed with dilute aqueous sodium hydroxide (2 × 50 ml), water (2 × 30 ml), and brine (2 × 30 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give an oil, which was distilled. The fraction b.p. 108—112 °C/0.02 mmHg solidified and was recrystallised from light petroleum, b.p. 40—60 °C, to give the *ester* (17.1 g, 67%) as prisms, m.p. 40—41 °C, R_F (B) 0.60, $\nu_{max.}$(Nujol mull) 1 735 cm^{-1} (C=O); δ($CDCl_3$) 7.1—7.5 (10 H, m, Ph and PhS), 4.12 (1 H, s, $CHCO_2Me$), and 3.62 (3 H, s, CO_2Me) (Found: M^+, 258.0709. $C_{15}H_{14}O_2S$ requires *M*, 258.0714); *m*/*z* 258 (M^+, 70%), and 199 (100, $M - CO_2Me$).

1-*Methyl Hydrogen* 2-*Phenyl*-2-*phenylthiosuccinate.*—Lithium di-isopropylamide (LDA) was prepared from di-isopropylamine (10.1 g) and BuLi (1.55M solution in hexane; 65 ml). This solution of LDA (10 ml) was added to a stirred solution of the above ester (2.6 g, 10 mmol) in THF (25 ml) at 0 °C under nitrogen. Separately, this solution of LDA (11 ml) was added to iodoacetic acid (2.1 g, 1 mmol) in THF (25 ml) at 0 °C under nitrogen. After 30 min the solutions were mixed and left at room temperature for 48 h. Water was added, the THF layer was separated, and the basic aqueous layer extracted with chloroform (2 × 30 ml). The combined organic layers were dried ($MgSO_4$) and evaporated to give recovered starting material (1.3 g, 50%). The aqueous layer was acidified with dilute HCl and extracted with chloroform (3 × 20 ml), and the extracts dried ($MgSO_4$) and evaporated to give an oil which was purified by chromatography on silica, eluting with ether; recrystallisation of the product from light petroleum (b.p. 30—40 °C) and ether gave the *ester* (1.22 g, 41%) as needles, m.p. 131—133 °C, R_F (D) 0.75, $\nu_{max.}$ (Nujol) 3 600—3 200 (OH), 1 730 (CO_2Me), and 1 710 cm^{-1} (CO_2H); δ($CDCl_3$) 7.1—7.5 (10 H, m, Ph, PhS), 3.83 (3 H, s, CO_2Me), and 3.26 and 3.54 (2 H, ABq, *J* 16.5 Hz, $CH_2^*CO_2H$) (Found: M^+, 316.0763. $C_{17}H_{16}O_4S$ requires *M*, 316.0769); *m*/*z* 316 (M^+ 30%), 257 (10, $M - CO_2Me$), 207 (35, M – PhS, CO_2), 131 (80), 110 (70, $PhSH^+$), 109 (60, PhS^+), and 103 (100, $PhCCH_2^+$) (Found: C, 64.4; H, 5.05; S, 11.6. $C_{17}H_{16}O_4S$ requires C, 65.4; H, 5.10; S, 10.1%). The same method in the presence of TMEDA gave a 43% yield of the half ester.

4-*Phenyl*-4-*phenylthio*-4,5-*dihydrofuran*-2(3H)-*one* (**63g**).—The above half ester (632 mg, 2 mmol) in dry THF (5 ml) was added slowly to a vigorously stirred suspension of sodium hydride (50% dispersion in oil; 100 mg, excess) in dry THF (60 ml) under nitrogen. After 0.5 h, lithium aluminium hydride (40 mg, 1 mmol) was added portionwise with vigorous stirring. After 3 h the suspension was carefully acidified with dilute HCl and stirred for 3 h. The solution was partitioned between ether and water. The combined organic extracts were washed with water (2 × 15 ml), aqueous sodium hydrogen carbonate (2 × 15 ml), and brine (2 × 10 ml), and dried ($MgSO_4$). Solvent evaporation under reduced pressure and p.l.c. on silica eluting with ether–light petroleum (b.p. 40—60 °C) gave the *lactone* (170 mg, 32%) as plates, m.p. 109—110 °C [from ether–light petroleum (b.p. 40—60 °C)], R_F (B) 0.1, $\nu_{max.}$(Nujol) 1 780 cm^{-1} (C=O); δ($CDCl_3$) 6.8—7.5 (10 H, m, Ph and PhS), 4.48 and 4.69 (2 H, ABq, *J* 10 Hz, CH_2^*O), and 3.03 (2 H, s, CH_2CO_2) (Found: M^+, 270.0714. $C_{16}H_{14}O_2S$ requires *M*, 270.0716); *m*/*z* 270 (M^+, 35%), 161 (100, M – PhS), and 110 (50, PhSH).

Methyl 3-*Methyl*-4-*phenylthiobut*-2-*enoate* (**65d**; R = Me).—Toluene-*p*-sulphonic acid monohydrate (150 mg, 0.71 mmol) and benzene (10 ml) were heated together under reflux, under a nitrogen atmosphere in an apparatus fitted with a Dean-Stark water remover. After 3 h the apparatus was connected to allow the condensate to re-enter the reaction medium directly and the lactone (**63d**) (135 mg, 0.65 mmol) and dry methanol (30 mg, slight excess) added. After the solution had been heated under reflux for 6 days under a nitrogen atmosphere it was allowed to cool and diluted with ether (40 ml). The organic layer was washed with aqueous sodium hydrogen carbonate (2 × 20 ml), water (2 × 10 ml), and brine (2 × 15 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Preparative layer chromatography on silica, eluting with ether–light petroleum (b.p. 40—60 °C) gave the *ester* (**65d**; R = Me) as an oil (94 mg, 66%), R_F (B) 0.46, $\nu_{max.}$ (film) 1 715 cm^{-1} (C=O); $\delta(CDCl_3)$ 7.0—7.4 (5 H, m, PhS), 5.5—5.6 (1 H, m, C*H*=CHMe), 4.16 (*Z*) and 6.53 (*E*) (2 H, br s, CH_2SPh), 3.58 (*E*) and 3.52(*Z*) (3 H, s, CO_2Me), 2.24 (*E*) (3 H, d, *J* 1 Hz, *Me*C=CH), and 1.95 (*Z*) (3 H, d, *J* 1.7 Hz, *Me*C=CH) (Found: M^+, 222.0715. $C_{12}H_{14}O_2S$ requires *M*, 222.0715); *m/z* 222 (M^+, 100%), 191 (25, *M* − OMe), 190 (25, *M* − MeOH), 163 (30, *M* − CO_2Me), 113 (60, *M* − PhS), 110 (35, PhSH), and 109 (40, PhS^+).

The following were similarly prepared. *Methyl* 4-*phenylthiopent*-2-*enoate* (**63b**; R = Me). As an oil (64%), R_F (B) 0.35, *E*-isomer only, $\nu_{max.}$(film) 1 730 (C=O) and 1 655 cm^{-1} (C=C); $\delta(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 6.87 (1 H, dd, *J* 15.5, 8 Hz, C*H*=CHCO), 5.56 (1 H, dd, *J* 15.5, 1 Hz, CH=C*H*CO), 3.75—3.95 (1 H, m, CHSPh), 3.71 (3 H, s, CO_2Me), and 1.45 (3 H, d, *J* 7 Hz, *Me*CH) (Found: M^+, 222.0714. $C_{12}H_{14}O_2S$ requires *M*, 222.0707); *m/z* 222 (M^+, 45%), 191 (20, *M* − Me), 190 (22, *M* − MeOH), 163 (40, *M* − CO_2Me), 113 (70, *M* − PhS), 110 (100, PhSH), and 109 (45, PhS^+).

Methyl 3-*methyl*-4-*phenylthiopent*-2-*enoate* (**65h**; R = Me). As an oil (81%), R_F (B) 0.51, as a mixture of *E*- and *Z*-isomers, ratio 4:1, $\nu_{max.}$(film) 1 718 (C=O) and 1 645 cm^{-1} (C=C); $\delta(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 5.71 (*Z*) and 3.73 (*E*), (1 H, q, *J* 7 Hz, CHSPh), 5.66 (*Z*) and 5.50 (*E*) (1 H, br s, C=CHCO), 3.61 (*E*) and 3.54 (*Z*) (3 H, s, CO_2Me), 2.23 (*E*) and 8.09 (*Z*), [3 H, each d, *J* 1 (*E*), 1.5 (*Z*) Hz, *Me*C=CH], and 1.40 (3 H, d, *J* 7 Hz, CH*Me*) (Found: M^+, 236.0872. $C_{13}H_{16}O_2S$ requires *M*, 236.0872); *m/z* 236 (M^+, 35%), 127 (100 , *M* − PhS), 110 (60, PhSH), and 109 (50, PhS^+).

Ethyl 4-*phenylthiobut*-2-*enoate* (**65a**; R = Et). As an oil (74%), R_F (B) 0.50, *E*-isomer only, identical with a sample prepared by direct displacement from ethyl 4-bromocrotonate.

Methyl 3-*phenyl*-4-*phenylthiobut*-2-*enoate* (**65g**; R = Me). As an oil (87%), R_F (B) 0.40, a mixture of isomers X and Y (3:2) $\nu_{max.}$(film) 1 715—1 735 cm^{-1} (C=O); $\delta(CDCl_3)$ 7.0—7.5 (10 H, m, Ph and PhS), 6.77 (X), and 6.02 (Y) (1 H, s, CH=C), 4.58 (Y) and 3.80 (X) (2 H, s, $PhSCH_2$), 3.69 (X) and 3.62 (Y) (3 H, s, CO_2Me) (Found: M^+, 284.0871. $C_{17}H_{16}O_2S$ requires *M*, 284.0873); *m/z* 284 (M^+, 100%), 175 (45, *M* − PhS), and 115 (52, *M* − PhSH, CO_2Me).

Methyl 3-[(*phenylthio*)*methyl*]*pent*-2-*enoate* (**65e**; R = Me). After 6 days, as an oil (84%), R_F (B) 0.44, a mixture of isomers (X and Y) (4:3), $\nu_{max.}$(film) 1 780 (C=O) and 1 642 cm^{-1} (C=C); $\delta(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 5.65 (1 H, br s, CH=C), 4.19 (Y) and 3.60 (X) (2 H, s, $PhSCH_2$), 3.66 (X) and 3.63 (Y) (3 H, s, CO_2Me), 2.85 (X) and 2.44 (Y) (2 H, br q, *J* 7 Hz, CH_2Me), and 8.86 (Y) and 1.0 (X) (3 H, t, *J* 7 Hz, CH_2Me) (Found: M^+, 236.0871. $C_{13}H_{16}O_2S$ requires *M*, 236.0875); *m/z* 236 (M^+, 100%), 202 (55, *M* − MeOH), 127 (65, *M* − PhS), 110 (45, PhSH), and 109 (40, PhS^+); stopping the above reaction after less time gave varying amounts of by-product, *methyl* 3-[(*phenylthio*)*methyl*]*pent*-3-*enoate* (**67**; R^2 = H, R = Me) as an oil, R_F (B) 0.37, a mixture of isomers (X and Y) (3:2), $\nu_{max.}$(film) 1 738 cm^{-1} (C=O); $\delta(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 5.59 (1 H, br q, *J* 6.5 Hz, CH=C), 3.80 (5 H, br s, $PhSCH_2$, CO_2Me), 3.39 (X) and 3.31 (Y) (each 2 H, br s, CH_2CO_2Me), and 1.79 (3 H, br d, *J* 6.5 Hz, *Me*CH=C) (Found: M^+, 236.0871. $C_{13}H_{16}O_2S$ requires *M*, 236.0889); *m/z* 236 (M^+, 100%), 127 (80, *M* − PhS), 110 (72, PhSH), and 109 (30, PhS^+).

5,5-*Dimethyl*-4-[(*phenylthio*)*methyl*]*dihydrofuran*-2(3H)-*one* (**71**).—The rearrangement of lactone (**63f**) as above gave the lactone (**71**) (83%) as an oil, R_F (C) 0.31, $\nu_{max.}$(film) 1 580 cm^{-1} (C=O); $\delta(CDCl_3)$ 7.2—7.4 (5 H, m, PhS), 2.3—3.3 (5 H, m, $PhSCH_2^*CH_2^*CO_2$), and 1.51 and 1.35 (2 × 3 H, each s, Me_2CO) (Found: M^+, 236.0884. $C_{13}H_{16}O_2S$ requires *M*, 236.0889); *m/z* 236 (M^+, 100%), 123 (80, $PhSCH_2^+$), 110 (40, PhSH), and 109 (15, PhS^+).

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