Reactions of α- or γ-Phenylthio Substituted Extended Enolate Anions Derived from Esters

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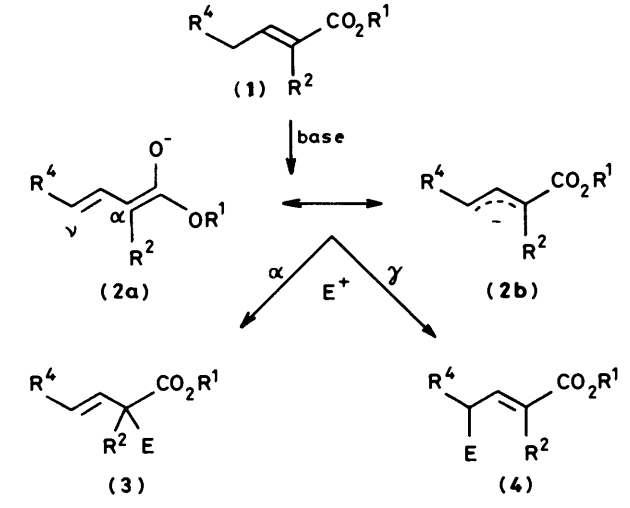
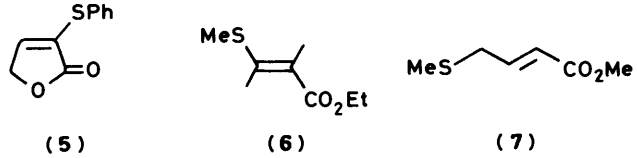
The title anions are alkylated and acylated (α series only) exclusively at the α position. The α-phenylthio products give γ-phenylthio compounds by the [1,3]PhS shift and the PhS group may be removed from the products in a number of ways.

Extended enolates[1-7] (**2**) derived from unsaturated esters (**1**) usually react with electrophiles such as alkyl halides,[1-4,7-18] aldehydes,[5] Michael acceptors,[17,18] and sulphenylating agents,[3,19,20] at the α carbon atom to give (**3**) though selectivity is far from complete.[5] Predictions in this area are hazardous: some compounds, notably those with an alkyl group at C-3, react α with alkyl halides, but γ with aldehydes[9,21] or allyl halides.[8] In this behaviour extended enolates resemble allyl anions and they can indeed be regarded as allyl anions unsymmetrically substituted with the strongly anion-stabilising carbonyl group (**2b**). The reasons for α-selectivity are not fully understood[22] but it is kinetic in origin as the γ product (**4**) is more stable, and higher temperatures do sometimes give more γ product from aldehydes.[5] The γ product is best approached[3] *via* silylated versions of (**2**).



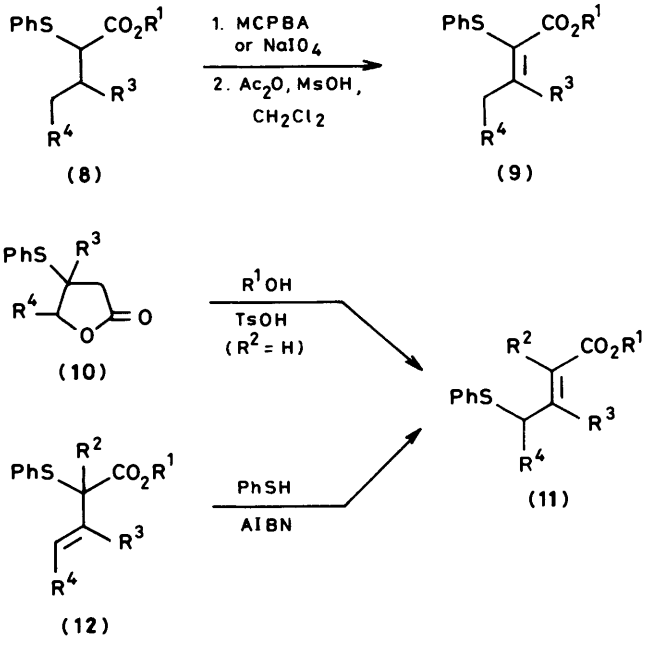
(1) (2a) (2b) (3) (4)

Some extended enolates with α, β, or γ RS substituents have been used. The anion of one unsaturated α-phenylthio lactone is methylated at the α-position,[23] though the α-phenylthio butenolide[23] (**5**) reacts with cyclopentanone at the γ carbon atom, but this may be an atypical result as enolates of butenolides have furan character.[24] The β-methylthio substituent in (**6**) has been used[25] to direct extended enolate reactivity to the position, and γ-methylthio compounds, such as (**7**), have been alkylated[26] and acylated,[27] usually in the α position, *via* their extended enolates. The corresponding sulphoxides[4] and sulphones[4,28] form successively more stable extended enolate ions which give successively more γ alkylation.



(5) (6) (7)

Modification of extended enolates by PhS substituents at the α or γ carbon atoms offers synthetic methods with greater control as PhS stabilises anions, conveys flexibility in allyl anion behaviour,[29] migrates by photochemical [1,3]PhS shifts,[30] perhaps thereby relating the α and γ series, and can easily be removed from the organic molecule when its work is done, leaving another functional group behind or not as the case may be. The relatively few reports of such modifications reflect the absence of general methods for preparing the starting materials. These are now available: the α-phenylthio compounds (**9**) can be made by a Pummerer-style dehydration[31,32] from the saturated sulphides (**8**) and the γ-phenylthio compounds (**11**) by [1,2]PhS migration[33,34] from the lactones (**10**) or by a [1,3]PhS shift from esters of 2-phenylthioalk-3-enoic acids[35,36] (**12**), and we now describe the formation and reactions of extended enolates derived from (**9**) and (**11**).†



(8) (9) (10) (11) (12)

Extended Enolates from the α-Phenylthio Compounds (**9**).—Another reason why so few anions from the esters (**9**) have been described is that they are excellent Michael acceptors[17,23,37] and potential bases, even lithium di-isopropylamide (LDA),[2] often prefer to add as nucleophiles. We find butyl-lithium

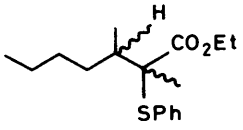
† Throughout the paper, R^{1-4} refer to substituents on C-1 to C-4 respectively.

Table 1. Deconjugation experiments on the esters (9)

Starting material				Product ratio	Stereo	Yield
	R^1	R^3	R^4	(15):(9)	(15)	(15) (%)
(9a)	Et	H	H	3:1	—	4[a]
(9b)	Me	Me	H	6:1	—	*b*
(9c)	Me	H	Me	1:1	*E*	47
(9d)	Me	H	Et	—	—	—
(9e)	Me	$-(CH_2)_3-$		2:1	—	38

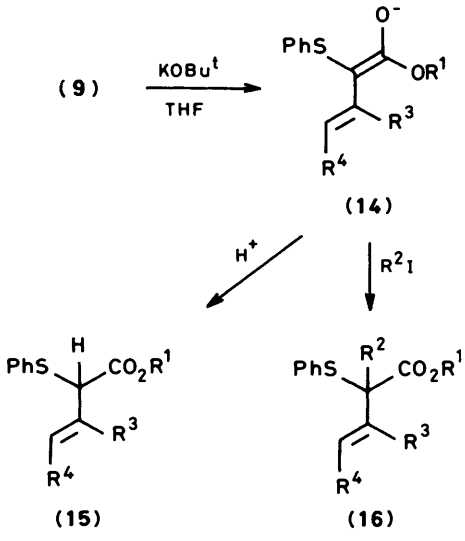
[a] Product (15a) is converted into (9a) on silica. [b] No separation, n.m.r. experiment.

(BuLi) adds in this way: addition of BuLi to ester (9a) followed by an excess of MeI gave only the Michael adduct (13) in 75% yield.



(13)

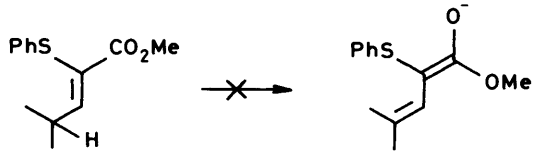
Other bases [NaH, Bu^{t}OK, or LDA on (9a)] followed by MeI gave complex mixtures of products containing no alkylated product (16). Lithium bis(trimethylsilyl)amide added to (9a) followed by MeI gave *ca.* 10% of (16). Addition of the ester to the same base gave *ca.* 20% (16) and the same inverse addition procedure with LDA gave (16) in 26% yield. Finally, we found that inverse addition of the ester (9a) to Bu^{t}OK in tetrahydrofuran (THF) at −78 °C and addition of MeI to the resulting anion (14) gave the ester (16aa) in 87% yield and we used this procedure for the other alkylations. We failed to make the anion (18) from the branched-chain ester (17) under these conditions; presumably the $A^{1,3}$ strain[38] is too great.



Quenching the anion (14) with $NaHCO_3$ gave the deconjugated esters (15) with some conjugated esters (9) (Table 1), suggesting kinetic protonation at the α carbon and some equilibration back to the more stable starting material. The deconjugated esters (15) were separated by chromatography, though only a poor yield of (15a) could be isolated as SiO_2 catalyses the reconjugation to give (9a).

Table 2. Alkylation of α-phenylthio extended enolates (14)

Ester	R^2	Electrophile	Product	Yield (%)	Stereo
(9a)	Me	MeI	(16aa)	87	—
	$PhCH_2$	$PhCH_2Br$	(16ab)	76	—
	allyl	$CH_2{=}CHCH_2Br$	(16ac)	34	—
(9b)	Me	MeI	(16ba)	96	—
	Et	EtI	(16bb)	94	—
	$PhCH_2$	$PhCH_2Br$	(16bc)	98	—
	$Pr^i(CH_2)_2$	R^2I	(16bd)	78	—
	Pr^i	Pr^iI	—	0	—
(9c)	Me	MeI	(16ca)	66	*E*
	Bu^t	Bu^{t}Br	(15c)	74	*E*
(9d)	Me	MeI	(16da)	82	*E*
	Et	EtI	(16db)	87	*E*
(9e)	Me	MeI	(16ea)	68	—
		+TMEDA, −78 °C	(16ea)	83	—
		+TMEDA, −20 °C	(16ea)	73	—



(17) (18)

Alkylations of the same anions were successful (Table 2) with primary alkyl iodides (Me, Et, and $Pr^iCH_2CH_2$) and benzyl or allyl bromides, but Pr^iI gave a complex mixture of products with (14b) and Pr^iCH_2Br gave a good yield of the deconjugated ester (15c) from the anion (14c), which presumably acts as a base to eliminate HBr. High yields of the alkylated products (16) were obtained with all the substitution patterns (9a—e) [though not of course with (17)]. Addition of *N,N,N,N*-tetramethylethylenediamine (TMEDA) to the pre-formed anion improved the yield of methylated product in one case [from 68 to 83% with (9e)] and raising the temperature to −20 °C gave only a small loss of yield (to 73% in the same case).

No traces of γ alkylated products were detected. Evidently the PhS group reinforces the natural directing effect of CO_2R, which is reasonable for an extended enolate as PhS is anion-stabilising, and CO_2R reinforces the natural α directing effect of PhS when (14) is considered as an allyl anion. These results also agree with Still and Macdonald's useful rule of thumb for allyl anions.[39] In their terms, PhS is a 'mild anion-stabilising' group. The PhS group also prevents the double alkylation often observed with simple derivatives.[40]

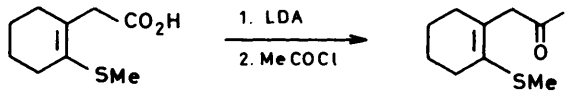
Where the double bond in the product has a geometry, it is produced in the *E* form only [(15c), (16c), and (16d)]. This is in marked contrast to the results with simple unsaturated esters: protonation[6] or alkylation[7] of (2) gives predominantly the opposite geometry (*E* or *Z*) from that of the starting ester (1). This result agrees with the suggestion[7] that, in these anions (2), $A^{1,2}$ strain is greater than $A^{1,3}$ strain as in our esters the extra PhS group greatly increases $A^{1,3}$ strain—enough to prevent the formation of one extended enolate (18).

Acylation of extended enolates usually occurs at oxygen,[41] and provides a standard preparation of 1-acyloxybutadienes for Diels–Alder reactions.[42,43] Silylation too occurs at oxygen[3] confirming that atom as the site of highest charge density in the extended enolate (2). There is one report[27] of the *C*-acylation of a γ-methylthio extended enolate, though admittedly on the dianion of the acid (19), a rather special case, and we investigated the acylation of our α-phenylthio extended enolates (14)

Table 3. Acylation of α-phenylthio extended enolates (**14**)

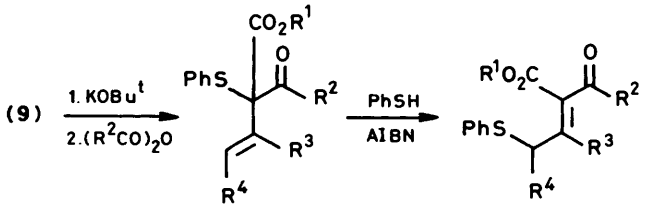
Ester	Acylating agent	t/°C	Product	Yield (%)
(**9a**)	AcCl	−78	(**20aa**)	37
	Ac_2O	−78	(**20aa**)	58
	PhCOCl	−78	(**20ab**)	52
	$(PhCO)_2O$	−78	(**20ab**)	76
(**9c**)	Ac_2O	−20	(**20ca**)	61
	$(PhCO)_2O$	−20	(**20cb**)	74
(**9e**)	Ac_2O	−78	(**20ea**)	55
	$(PhCO)_2O$	−78	(**20eb**)	74

in the hope that PhS would direct acylation to carbon rather than oxygen by a steric or electronic effect.



(**19**)

Initial experiments with MeCOCl and PhCOCl on the simplest anion (**14a**) were promising as keto esters (**20**) were formed, though in only moderate yield (Table 3). The anhydrides Ac_2O and $(PhCO)_2O$ gave better yields, and the best conditions seemed to be −20 °C rather than the −78 °C used for the alkylations. The products had two i.r. carbonyl stretching frequencies at *ca.* 1 740 and 1 700 cm^{-1}, for ester and ketone, and lacked an absorption for an enol ether. No trace of *O*- or γ-acylation was observed. Products from (**9c**) were *E* isomers only, suggesting that $A^{1,3}$ strain is again an important factor, and it may be that *C*-acylation is preferred to *O*-acylation as the latter would increase $A^{1,3}$ strain.



(**20**) (**21**)

Transposition of α*-Phenylthio Products* (**16**) *and* (**20**) *into* γ*-Phenylthio Compounds* (**27**) *and* (**21**) *by* [1,3]PhS *Shifts*.—The [1,3]PhS shift [(**22**)—(**23**)] can be catalysed[30] by light, heat,

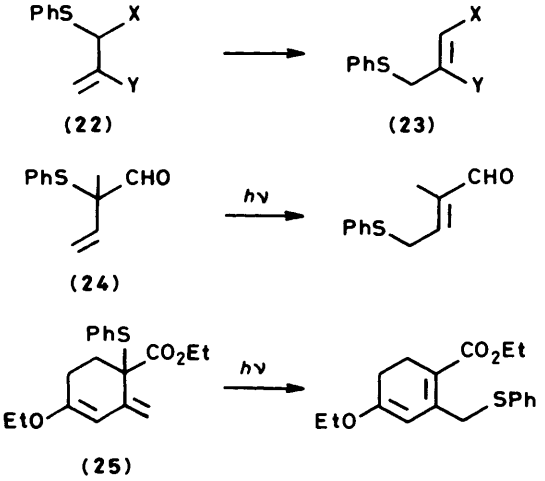


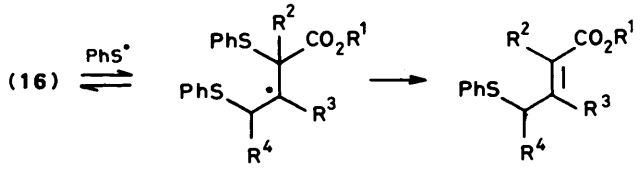
Table 4. The [1,3]PhS Shift

Starting material					Product		
	R^1	R^2	R^3	R^4		Yield (%)	Geometry
(**15a**)	Et	H	H	H	(**28a**)	100[a]	*E*
(**16aa**)	Et	Me	H	H	(**27aa**)	*a*	*E*
(**16ab**)	Et	$PhCH_2$	H	H	(**27ab**)	94	*Z*:*E* 15:85
(**16ac**)	Et	allyl	H	H	(**27ac**)	*a*	Mixture
(**15b**)	Me	H	Me	H	(**28b**)	*a*	Mixture
(**16ba**)	Me	Me	Me	H	(**27ba**)	96	*Z*:*E* 3:4
(**16bb**)	Me	Et	Me	H	(**27bb**)	*a*	Mostly *E*
(**16bc**)	Me	$PhCH_2$	Me	H	(**27bc**)	*a*	*Z*:*E* 1:2
(**16da**)	Me	Me	H	Et	(**27da**)	100[a]	Mostly *E*
(**16db**)	Me	Et	H	Et	(**27db**)	92	*Z*:*E* 18:82[b]
(**16ea**)	Me	Me	$-(CH_2)_3-$		(**27ea**)	100	*Z*:*E* 1:1
(**20ab**)	Et	PhCO	H	H	(**21ab**)	56	*Z*:*E* 1:1
(**20cb**)	Me	PhCO	H	Me	(**21cb**)	56	*Z*:*E* 1:1
(**20ea**)	Me	MeCO	$-(CH_2)_3-$		(**21ea**)	53	*Z*:*E* 1:1

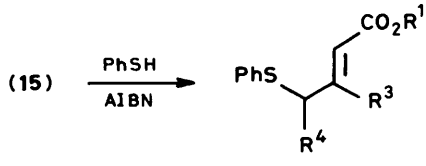
[a] N.m.r. experiment; product not isolated. [b] *E* and *Z*-Isomers separated by h.p.l.c.

acid (X = aryl), or by addition of PhSH (to provide PhS·). We and others[44] believe the light, heat, and PhS·-catalysed reactions to be radical chain processes though Kwart[45] has evidence that it is a pericyclic reaction. It occurs readily in laboratory light for simple sulphides[46,47] (X, Y = alkyl), easily[48] when X or Y is Ph_2PO, and very easily[49] when X = PhS. The β,γ-unsaturated aldehyde[50] (**24**) and ester[20] (**25**) undergo the [1,3]PhS shift in daylight.

To our surprise, the α-phenylthio products (**16**) and (**20**) were very reluctant to undergo the [1,3]PhS shift to give (**27**) and (**21**) on exposure to daylight, or the u.v. source used to inspect t.l.c. plates (254 nm), or on treatment with a catalytic amount of PhSH. After 4 weeks in sunlight, only 24% of the α-phenylthio compound (**20ab**) had isomerised to the γ-phenylthio compound (**21ab**). Evidently the carbonyl group suppresses photochemical initiation, perhaps by interaction with the double bond across space.[51]



(**26**) (**27**)



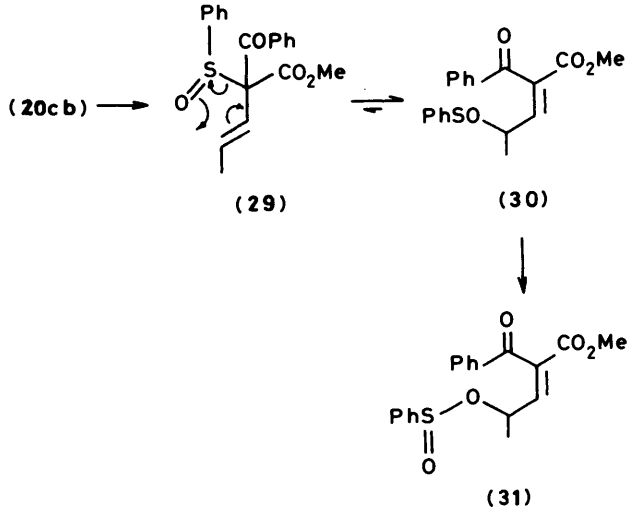
(**28**)

Initiation by PhS·, generated from PhSH with azoisobutyronitrile (AIBN) in refluxing benzene or CCl_4 did convert the esters (**16**) and (**15**) into the γ-phenylthio compounds (**27**) and (**28**) in essentially quantitative yield, presumably *via* the radical (**26**), and the keto esters (**20**) into (**21**) in moderate yield (Table 4). It is clear that each additional carbonyl group at the migration origin makes the [1,3]PhS shift more difficult but it is not clear why. The reserve is true for the pericyclic [2,3] sigmatropic shift involved in the Evans-Mislow rearrangement,[29] *e.g.* (**29**) to (**30**), as attempted conversion of (**20cb**) into

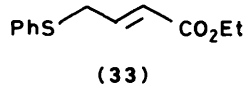
Table 5. Reactions of the γ-phenylthio extended enolates (36)

Starting material	Electrophile	Product	R^1	R^2	$R^{2'}$	R^3	R^4	Yield (%)	Stereo
(33)	$NaHCO_3$	(37a)	Et	H	H	H	H	89	*E*
(34)	$NaHCO_3$	(37b)	Bu	H	H	H	Me	95	Mixture
(34)	MeI	(38a)	Bu	Me	H	H	Me	84	Mixture
(27ab)	MeI	(38b)	Et	$PhCH_2$	Me	H	H	91	*E*:*Z* 7:1
(27ab)	EtI	(38c)	Et	$PhCH_2$	Et	H	H	89	*E*
(27db)	MeI	(38d)	Me	Et	Me	H	Et	88	*E*:*Z* 6:1
(34)	MeI	(39a)	Bu	Me	Me	H	Me	83	*E*:*Z* 9:1
(34)	EtI	(39b)	Bu	Et	Et	H	Me	88	*E*
(34)	PrI	(39c)	Bu	Pr	Pr	H	Me	79	*E*

the sulphoxide (29) with *m*-chloroperbenzoic acid (MCPBA) gave instead the rearranged sulphinate ester (31). Evidently the equilibrium in the [2,3] sigmatropic shift is entirely on the side of the sulphenate ester (30) which is oxidised to (31) by MCPBA. The ester was formed as a 1:1:1:1 mixture of isomers. Treatment of (16ab) with 1 equivalent of the milder oxidising agent $NaIO_4$ gave 50% (16ab) and a 50% yield of the rearranged sulphinate ester (32) confirming the remarkable ease of the [2,3] shift.



Extended Enolates from the γ-Phenylthio Compounds (11).—Anions from a few γ-RS compounds have been studied,[4,27] notably by Kende,[26] who alkylated the anion of γ-methylthiocrotonate (7) in the α position and used the products in a number of syntheses. We have studied anions from the esters (33), (34), and (35), made by rearrangement[33,34] of the corresponding lactones (10), and from the esters (27ab) and (27db) made by [1,3]PhS shifts from (16).



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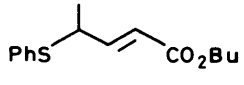

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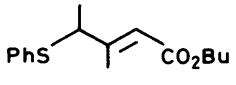
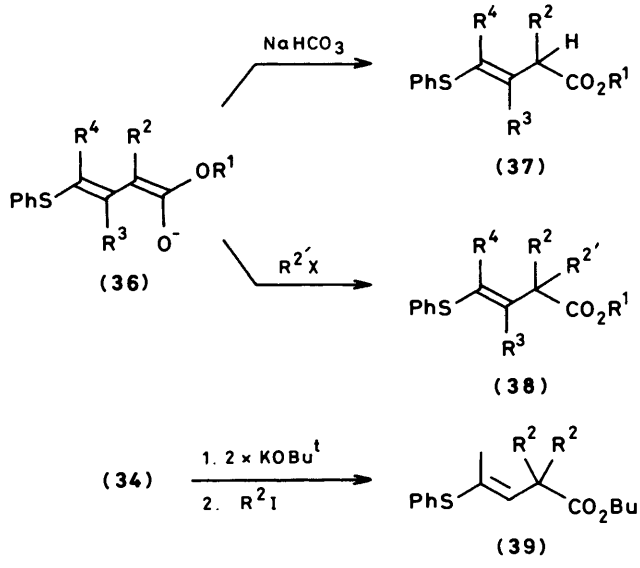


(35)

Anions (36) from these esters are easier to form than those from the α-phenylthio compounds (9) as there is less tendency for Michael addition and the γ-PhS group enhances the acidity of the γ protons. We found the same base system (KOBu^t, THF) suitable, but inverse addition and low temperatures were not necessary.



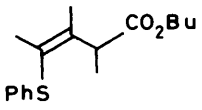
The anions (36) may be captured by a proton (supplied by $NaHCO_3$) to give the non-conjugated esters (37) (Table 5) in good yield with no contamination by starting material. The PhS group strongly attracts double bonds,[52] so kinetic and thermodynamic factors probably favour (37).

Monoalkylation of the ester (34) was achieved in two ways. Treatment with LDA and MeI gave *ca.* 50% α-methylated product (38) with other apparently monomethylated products. Addition of the co-solvents hexamethylphosphoramide (HMPA) or TMEDA improved the yield to 77 and 83% respectively. Alternatively, KOBu^t and MeI gave 84% (38) with 5% (34) and 10% dimethylated product (39; R = Me) which were separated by p.l.c. Compounds of this sort are better approached by alkylation of the α-phenylthio compounds (9) and subsequent [1,3]PhS shift [(27; R^1 = Bu, R^2 = R^4 = Me, R^3 = H) has the same skeleton as (38)].

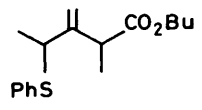
Even compounds (27ab) and (27db), which already had an alkyl group at C-2, formed anions which were alkylated again at that same site: the yields were excellent (Table 5) and no trace of γ- or polyalkylated products were found. These results extend Kende's observations on the unsubstituted compound (7) and suggest that the α-directing ester group dominates the reactivity of the extended enolates (36) with perhaps some thermodynamic assistance from the PhS group.

One compound proved troublesome. Alkylation of (35) using LDA and MeI gave a mixture of α-methylated products (40)—(42). The allyl sulphide (42) is derived from (41) by a [1,3]PhS shift and (41) comes from an extended enolate ion (43) formed without the anion-stabilising effect of the PhS group. An

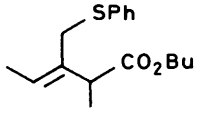
attempt to equilibrate (**43**) to the presumably more stable (**36**; R^1 = Bu, R^2 = H, R^3 = R^4 = Me) using KOBu^t gave more (**40**) but the time allowed for the equilibration caused some decomposition and some dialkylation also occurred. Compounds of this substitution pattern are again better approached by α-alkylation of the α-phenylthio compound (**9**) and a [1,3]PhS shift.



(**40**)



(**41**)



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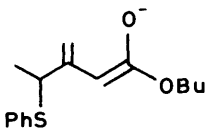
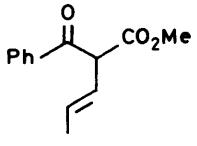
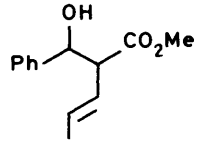


(**43**)

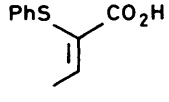
Removal of Sulphur from the Products.—Some reactions are well established. Reductive removal[25] of sulphur with Raney nickel replaces PhS by H. Those products which are vinyl sulphides, *i.e.* (**37**), (**38**), and (**39**), can be hydrolysed[26,27,50] to the corresponding aldehydes or ketones. We have already referred to the Evans-Mislow rearrangement which gives allylic alcohols[19,53,54] from the α-alkylated products (**16**); thermal elimination on the same intermediates, *cf.* (**31**) and (**32**), gives alka-2,4-dienoic acids.[55] Other useful transformations have been described by Uda.[54] We have, therefore, attempted the removal of PhS only from the least known of our products, the keto esters (**21**).



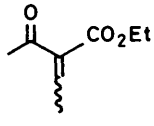
(**44**)



(**45**)



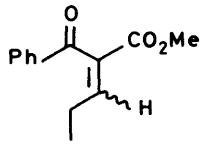
(**46**)



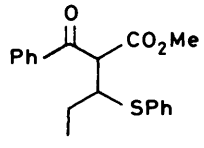
(**47**)

Treatment of (**20aa**) with lithium in liquid ammonia immediately discharged the blue colour of the reagent, but quenching the red solution with MeI gave only a trace of (**16aa**). Aluminium amalgam[56] has been used to remove a PhS group from α-phenylthio ketones,[57] and gave the desulphurised keto ester (**44**) from (**20cb**) after 10 min and the hydroxy ester (**45**) after 5 h. Reduction of aromatic ketones by this reagent is known.[58] The double bond remained out of conjugation in both these products. Compounds of this kind have been made by Kende[7] from simple extended enolates.

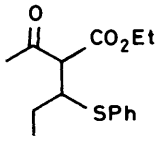
Compounds (**20**) have a non-enolisable PhS-substituted carbon atom between two β-related CO groups and are very easily fragmented by base.[59] Treatment of (**20aa**) with NaOH solution hydrolysed the ester and deacetylated the compound to give the acid (**46**) as the only isolated product. Trimethylsilyl iodide[60] desulphurised (**20aa**) to give both isomers of the conjugated ester (**47**) and diphenyl disulphide. This reagent has been used[61] to hydrolyse β-keto esters but in this case the soft iodide ion must attack sulphur rather than the ethyl group.



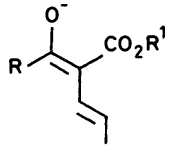
(**48**)



(**49**)



(**50**)



(**51**)

The PhS group may also be removed by the more common thiophile PhS^-. Treatment of (**20cb**) with equimolar amounts of PhSH and NaOH gave a mixture of (**44**), (**48**), and (**49**), the product of Michael addition of PhS^- to (**48**). Two equivalents of NaOH and *three* of PhSH gave predominantly (**48**), while two of NaOH and *four* of PhSH gave (**49**) from (**20cb**) and (**50**) from (**20aa**). In these reactions, the first molecule of PhS^- must act as a thiophile, releasing the extended enolate (**51**) which is protonated α to give (**44**) which, in turn, equilibrates in base to (**48**). Any excess of PhSH is scavenged by (**48**) to give (**49**).

Experimental

General experimental details have been reported.[61] Starting materials were prepared by the methods of the previous paper.[32] T.l.c. solvent systems (A), (B), and (C) are given in the previous paper.[32] In ^{13}C n.m.r. spectra, peaks marked with an asterisk belong to *ortho* or *meta* carbon atoms and are of double intensity.

Ethyl 2,3-Dimethyl-2-phenylthioheptanoate (**13**).—BuLi (1.55M solution in hexane; 1 ml, 1.5 mmol) was added to a stirred, cooled (−78 °C) solution of ethyl 2-phenylthiobut-2-enoate (335 mg, 1.5 mmol) in dry THF (3 ml) under a nitrogen atmosphere. After 10 min, methyl iodide (0.4 g, excess) in dry THF (1 ml) was added and the mixture stirred for 10 min at −78 °C, and then left to attain room temperature (2—3 h). The resultant suspension was diluted with ether (20 ml), washed with water (2 × 10 ml) and brine (2 × 10 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure. P.l.c. gave the *ester* (334 mg, 75%), a mixture of diastereoisomers, as an oil, R_F(A) 0.44, 0.42, $\nu_{max.}$ 1 735 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 3.9—4.2 (2 H, m, CO_2CH_2Me), 1.9—2.2 (1 H, br m, $MeCHCH_2$), 1.31 (3 H, s, PhS*Me*), and 0.8—1.5 (13 H, m, other CHs) (Found: M^+, 294.1649. $C_{17}H_{26}O_2S$ requires *M*, 294.1653); *m/z* 294 (90%), 221 (100, *M* − CO_2Et), and 185 (75, *M* − PhS).

Ethyl 2-Methyl-2-phenylthiobut-3-enoate (**16aa**).—Ethyl 2-phenylthiobut-2-enoate (**9a**) (0.95 g, 4.3 mmol) in dry THF (*ca.* 2M-solution; 2 ml) was added dropwise to a stirred, cooled (−78 °C) solution of potassium t-butoxide (0.58 g, 5.2 mmol) in dry THF (*ca.* 0.5M-solution; 11 ml) under a nitrogen atmosphere. The yellow solution was stirred at −78 °C for 0.5 h and then quenched with methyl iodide (1 g, slight excess) in dry THF (*ca.* 2M-solution; 3 ml); it was then stirred whilst slowly warming to room temperature (4—5 h). The solution

was diluted with ether (100 ml), washed with water (2 × 20 ml) and brine (2 × 20 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the product (shown by n.m.r. to contain <5% of the starting material). P.l.c. gave the *ester* (0.875 g, 87%) as an oil R_F(A) 0.40, $\nu_{max.}$(liq.) 1 735 cm^{-1} (C=O); δ_H($CDCl_3$) 7.1—7.5 (5 H, m, PhS), 6.23 (1 H, dd, *J* 10, 18 Hz, C*H*=CH_2), 5.16 (1 H, d, *J* 10 Hz and 1 H, d, *J* 18 Hz, CH=CH_2), 4.11 (2 H, q, *J* 7 Hz, OCH_2Me), 1.58 (3 H, s, Me), and 1.21 (3 H, t, *J* 7 Hz, OCH_2*Me*) (Found: M^+, 236.0871. $C_{13}H_{16}O_2S$ requires *M*, 236.0864), *m/z* 236 (18%), 209 (80, *M* − CH=CH_2), 163 (70, *M* − CO_2Et), 135 (85, *M* − H, CH=CH_2, CO_2Et), 110 (100, $PhSH^+$), and 109 (91, PhS^+). The following were prepared from ethyl 2-(phenylthio)but-2-enoate in the same way.

Ethyl 2-benzyl-2-phenylthiobut-3-enoate (**16ab**). The *ester* (76%) was an oil, R_F(A) 0.28, $\nu_{max.}$(liq.) 1 730 cm^{-1} (C=O); δ_H($CDCl_3$) 7.0—7.5 (10 H, m, Ph and PhS), 6.1 (1 H, dd, *J* 17.5, 10.5 Hz, C*H*=CH_2), 5.1—5.5 (2 H, m, CH=CH_2), 3.95 (2 H, q, *J* 7 Hz, OCH_2Me), 3.50 and 3.20 (2 H, AB system, *J* 13 Hz, PhCH_2), and 1.07 (3 H, t, *J* 7 Hz, OCH_2*Me*) (Found: M^+, 312.1184. $C_{19}H_{20}O_2S$ requires *M*, 312.1199), *m/z* 312 (40%), 221 (55, *M* − CH_2Ph), 129 (100, *M* − PhS, H, CO_2Et), 110 (38, $PhSH^+$), and 109 (27, PhS^+).

Ethyl 2-propenyl-2-phenylthiopent-4-enoate (**9ac**). The *ester* (34%) was an oil, R_F(A) 0.31, $\nu_{max.}$(liq.) 1 734 (C=O) and 1 640 cm^{-1} (C=C); δ_H($CDCl_3$) 7.1—7.5 (5 H, m, PhS), 4.8—7.3 (6 H, m, vinyl Hs), 4.13 (2 H, q, *J* 7 Hz, OCH_2Me), 2.72 (2 H, br d, *J* 6.5 Hz, CH_2^*CH=CH_2), and 1.20 (3 H, t, *J* 7 Hz, OCH_2*Me*) [Found: M^+, 221.0637. $C_{12}H_{13}O_2S$ (=*M* − CH_2CH=CH_2) requires 221.0641], *m/z* 262 (50%), 221 (55, *M* − CH_2CH=CH_2), 189 (55, *M* − CO_2Et), 147 (90, *M* − H, CH_2CH=CH_2, CO_2Et), 110 (100, $PhSH^+$), and 109 (79, PhS^+).

Ethyl 2-Phenylthiobut-3-enoate (**15a**).—Quenching the anion prepared as above with aqueous sodium hydrogen carbonate gave a mixture of ethyl 2-phenylthiobut-2-enoate (the starting material) and the ester, R_F(A), (B) one spot same as starting material. N.m.r. showed a ratio of 1:4 for the starting material:product, purification by column chromatography on silica, eluting with 5% ether in light petroleum (b.p. 30—40 °C) gave 4% of (**15a**) R_F(CH_2Cl_2) 0.57; $\nu_{max.}$(film) 1 740 cm^{-1} (CO_2Me), δ_H($CDCl_3$) 7.1—7.5 (5 H, m, PhS), 5.99 (1 H, dd, *J* 9.5, 18 Hz, C*H*=CH_2), 5.22 (2 H, 2 br d, *J* 9.5, 18 Hz, CH=CH_2), 4.4—4.1 (1 H, m, PhSC*H*CO_2Et), 4.16 (2 H, q, *J* 7 Hz, OCH_2Me), and 8.71 (3 H, t, *J* 7 Hz, OCH_2*Me*); *m/z* 222 (40%, M^+), 149 (100, *M* − CO_2Et), 110 (40, PhSH), and 69 (40, C_4H_5O), 60% starting material, and 4% (*E*)-ethyl 4-phenylthiobut-2-enoate (**28a**). Also prepared in a similar manner were the following.

(E)-*Methyl 2-phenylthio-3-pentenoate* (**15c**). The ester (**9c**) gave a mixture of the deconjugated ester (**15c**) and starting material (**9c**) in a ratio of 1:1 by n.m.r. spectroscopy. Purification by column chromatography on silica gel eluting with 5% ether in light petroleum (b.p. 30—40 °C) gave the *ester* (117 mg, 47%) as an oil, R_F(CH_2Cl_2) 0.58; $\nu_{max.}$(film) 1 740 (CO_2Me), 1 590 (PhS), and 970 cm^{-1} (*trans*-HC=CH); δ_H(250 MHz, $CDCl_3$) 7.25—7.50 (5 H, m, PhS), 5.57—5.63 (2 H, m, CH=CH), 4.25—4.27 (1 H, m, PhSC*H*), 3.65 (3 H, s, MeO), and 1.67 (3 H, d, *J* 4 Hz, *Me*CH=CH) (Found: M^+, 222.0706. $C_{12}H_{14}O_2S$ requires *M*, 222.0715); *m/z* 222 (50%, M^+), 190 (25, *M* − MeOH), 163 (60, *M* − CO_2Me), 113 (80, *M* − PhS), 110 (50, PhSH), and 58 (100, Me_2CO).

Methyl 2-cyclopent-1-enyl-2-phenylthioacetate (**15e**). The ester (**9e**) gave a mixture of the deconjugated ester (**15e**) and starting material (**9e**) in a ratio of 2:1 by n.m.r. spectroscopy. Purification by column chromatography on silica gel eluting with 5% ether in light petroleum (b.p. 30—40 °C) gave the ester (this compound has been prepared before[62] but not fully characterised) (148 mg, 38%) as an oil, R_F(CH_2Cl_2) 0.63, *m/z* 248 (35%, M^+), 216 (20, *M* − MeOH), 189 (28, *M* − CO_2Me), 139 (78, *M* − PhS), 110 (100, PhSH), and 107 (76, *M* − PhS − MeOH).

(E)-*Methyl 2-Methyl-2-phenylthiohex-3-enoate* (**16da**).—Methyl 2-phenylthiohex-2-enoate (**9d**) (0.93 g, 4 mmol) in dry THF (2 ml) was added dropwise to a stirred, cooled (−78 °C) solution of potassium t-butoxide (0.54 g, 4.8 mmol) in dry THF (10 ml) under nitrogen. The yellow solution was stirred at −78 °C for 0.5 h and then quenched with methyl iodide (0.8 g, slight excess) in dry THF (2 ml); it was then stirred while slowly warming to room temperature (4—5 h). The suspension was diluted with ether (100 ml), washed with water (2 × 30 ml) and brine (2 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The product was purified by p.l.c. to give the *ester* (0.81 g, 82%) as an oil, R_F(A) 0.32; $\nu_{max.}$(liq.) 1 735 cm^{-1} (C=O), shown by n.m.r. to be the *E* isomer only; δ_H($CDCl_3$) 7.0—7.5 (5 H, m, PhS), 5.75 (1 H, d, *J* 16.5 Hz, C*H*:CH), 5.45 (1 H, d, *J* 16.5, 4.5 Hz, CH=C*H*CH_2), 3.59 (3 H, s, CO_2Me), 1.8—2.2 (2 H, m, CH_2Me), 1.5 (3 H, s, PhSC*Me*), and 0.92 (3 H, t, *J* 7 Hz, CH_2*Me*) (Found: M^+, 250.1027. $C_{14}H_{18}O_2S$ requires *M*, 250.1024); *m/z* 250 (15%), 141 (100, *M* − PhS), 110 (35, $PhSH^+$), and 109 (60, PhS^+). Also prepared in this way was the following.

Methyl 2-ethyl-2-phenylthiohex-3-enoate (**16db**). The *ester* (87%), *E*-isomer only, was an oil, R_F [1:20 ether–light petroleum (b.p. 30—40 °C)] 0.25, $\nu_{max.}$(liq.) 1 730 cm^{-1} (C=O); δ_H($CDCl_3$) 7.1—7.5 (5 H, m, PhS), 5.62 (2 H, br s, CH=CH), 3.61 (3 H, s, OMe), 1.7—2.2 (4 H, m, 2 × CH_2Me), and 0.13 and 0.89 (6 H, 2 t, *J* 7, 6.5 Hz, 2 × CH_2*Me*) (Found: M^+, 264.1184. $C_{15}H_{20}O_2S$ requires *M*, 264.1191); *m/z* 264 (18%), 155 (100, *M* − PhS), 110 (60, $PhSH^+$), and 109 (35, PhS^+).

Methyl 2,3-Dimethyl-2-phenylthiobut-3-enoate (**16ba**).—Methyl 3-methyl-2-phenylthiobut-2-enoate (**9b**) (0.74 g, 3.3 mmol) in dry THF (1.6 ml) was added dropwise to a stirred, cooled (−78 °C) solution of potassium t-butoxide (0.45 g, 4 mmol) in dry THF (8 ml) under nitrogen. The white suspension was stirred at −78 °C for 1 h and then quenched with methyl iodide (0.7 g, slight excess) in dry THF (2 ml); it was then stirred whilst the suspension warmed to room temperature slowly (3—4 h). The suspension was diluted with ether (100 ml), washed with water (2 × 30 ml) and brine (2 × 20 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the *ester* (0.758 g, 96%) as an oil, R_F(B) 0.48, $\nu_{max.}$(liq.) 1 740 (C=O) and 1 645 cm^{-1} (C=C); δ_H($CDCl_3$) 7.0—7.4 (5 H, m, PhS), 4.79 (1 H, br s, *trans*-C*H*=CMe), 4.68 (1 H, s, *cis*-C*H*=CMe), 3.54 (3 H, s, CO_2Me), 1.78 (3 H, br s, *Me*C=C), and 1.39 (3 H, s, PhSCMe) (Found: M^+, 236.0871. $C_{13}H_{16}O_2S$ requires *M*, 236.0870); *m/z* 236 (60%), 127 (90, *M* − PhS), 110 (100, $PhSH^+$), and 109 (65, PhS^+). Also prepared from methyl 3-methyl-2-phenylthiobut-3-enoate (**9b**) in this way were the following.

Methyl 2-ethyl-3-methyl-2-phenylthiobut-3-enoate (**16bb**). The *ester* (94%) was a colourless oil, R_F(A) 0.31, $\nu_{max.}$(liq.) 1 735 (C=O) and 1 640 cm^{-1} (C=C); δ_H($CDCl_3$) 7.65 (5 H, br s, PhS), 4.92 (1 H, br s, *trans*-C*H*=CMe), 4.70 (1 H, s, *cis*-C*H*=CMe), 3.68 (3 H, s, CO_2Me), 1.85 (3 H, br s, *Me*C=CH_2), 0.5—2.0 (2 H, m, CH_2^*Me), and 1.01 (3 H, m, CH_2^**Me*) (Found: M^+, 250.1008. $C_{14}H_{18}O_2S$ requires *M*, 250.1027); *m/z* 250 (40%), 141 (95, *M* − PhS), 110 (100, $PhSH^+$), and 109 (50, PhS^+).

Methyl 2-benzyl-3-methyl-2-phenylthiobut-3-enoate (**16bc**). The *ester* (98%) was an oil, R_F(A) 0.23, $\nu_{max.}$(liq.) 1 735 (C=O) and 1 640 cm^{-1} (C=C); δ_H($CDCl_3$) 7.0—7.6 (10 H, m, Ph and PhS), 4.90 (1 H, br s, *trans*-C*H*=CMe), 4.75 (1 H, s, *cis*-C*H*=CMe), 3.51 (3 H, s, CO_2Me), 3.25 (2 H, s, $PhCH_2$), and 1.85 (3 H, br s, *Me*C=CH_2) (Found: M^+, 312.1175. $C_{19}H_{20}O_2S$

requires *M*, 312.1184); *m/z* 312 (10%), 203 (45, *M* − PhS), 202 (40, *M* − H, PhS), and 143 (100, *M* − H, PhS, CO_2Me).

Methyl 5-methyl-2-phenylthio-2-prop-2-enylhexan-2-oate (**16bd**). The *ester* (78%) was an oil, R_F(A) 0.34, $\nu_{max.}$(liq.) 1 738 (C=O), and 1 640 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 7.3 (5 H, br s, PhS), 4.85 (1 H, br s, *trans*-C*H*=CMe), 4.72 (1 H, s, *cis*-C*H*=CMe), 3.67 (3 H, s, CO_2Me, (1.80 (3 H, br s, *Me*C=CH_2), and 0.5—2.2 (11 H, m, other CHs) (Found: M^+, 292.1455. $C_{17}H_{24}O_2S$ requires *M*, 292.1477); *m/z* 292 (40%), 183 (95, *M* − PhS), 123 (70, *M* − PhS, CO_2Me), 110 (100, $PhSH^+$), and 109 (60, PhS^+).

Methyl 3-Methyl-2-phenylthiobut-3-enoate (**15b**).—Quenching the anion from (**9b**) with aqueous sodium hydrogen carbonate gave a mixture of (**9b**) and the ester, R_F(A), (B) one spot, same as the starting material. No purification was attempted, n.m.r. spectroscopy indicated a ratio of 15:85 for starting material:product, (**15b**) had $\delta_H(CDCl_3)$ 7.0—7.5 (5 H, m, PhS), 4.85 (2 H, br s, CH_2), 4.29 (1 H, br s, PhSC*H*), 3.65 (3 H, s, CO_2Me), and 8.12 (3 H, br s, *Me*C=CH_2).

Oxidation of Ethyl 2-Benzyl-2-phenylthiobut-3-enoate (**16ab**).—The ester (0.3 g, *ca.* 1 mmol) was dissolved in methanol (20 ml) containing water (3 ml) and sodium metaperiodate (0.21 g, 1 mmol) in a foil-wrapped flask under nitrogen. After 48 h at room temperature the mixture was diluted with water (50 ml), and extracted with ether (3 × 20 ml). The organic extracts were washed with brine (2 × 15 ml), dried ($MgSO_4$), and evaporated under reduced pressure. N.m.r. spectroscopy indicated the product was *ca.* 50% starting ester and 50% sulphinate ester (**32**). P.l.c. gave *ethyl 2-benzyl-4-phenylsulphinyloxybut-2-enoate* as an oil (169 mg, 49%), a mixture of isomers (*E*:*Z*, 1:1), R_F(C) 0.30 [Found: M^+, 203.1072. $C_{13}H_{15}O_{21}$ (*M* − $PhSO_2$) requires *M*, 203.1069]; *m/z* 344 (2%) and 203 (100, *M* − $PhSO_2$); $\delta_H(CDCl_3)$ 6.9—7.5 (11 H, m, Ph, PhS and CH=C), 4.2—4.8 (2 H, m, $PhSO_2CH_2$), and 0.95—1.10 (3 H, m, CO_2CH_2Me).

(E)-*Methyl 2-Methyl-2-phenylthiopent-3-enoate* (**16ca**).—Methyl 2-phenylthiopent-2-enoate (**9c**) (174 mg, 1.55 mmol) in dry THF (1 ml) was added dropwise to a stirred solution of potassium t-butoxide (295 mg, 1.32 mmol) in dry THF (25 ml) under nitrogen at −78 °C. After 15 min, methyl iodide (220 mg, 0.1 ml, 1.5 mmol) in dry THF (1 ml) was added and the cooling bath removed. After 1 h the mixture was diluted with ether (25 ml), washed with water (2 × 10 ml) and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (50 g) eluting with 5% ether in light petroleum (b.p. 30—40 °C) to give the *ester* (204 mg, 66%, 71% based on recovered starting material), as an oil, $R_F(CH_2Cl_2)$ 0.6; $\nu_{max.}$(liq.) 1 735 (CO_2Me), 1 615 (C=C), 1 590 (Ph), and 970 cm^{-1} (*trans*-HC=CH); $\delta_H(CDCl_3)$ 7.3—7.6 (5 H, m, PhS), 5.95 (1 H, br d, *J* 15 Hz, MeCH=C*H*), 5.64 (1 H, dq, *J* 15, 6 Hz, MeC*H*=CH), 3.69 (3 H, s, MeO), 1.73 (3 H, d, *J* 6 Hz, *Me*CH=CH), and 1.58 (3 H, s, PhSC*Me*) (Found: M^+, 236.0894. $C_{13}H_{16}O_2S$ requires *M*, 236.0917); *m/z* 236 (20%, M^+), 222 (15, *M* − Me), 204 (15, *M* − MeOH), 177 (5, *M* − CO_2Me), 163 (5, *M* − MeOH − MeCH=CH), 127 (100, *M* − PhS), 110 (40, PhSH), and 95 (40, *M* − PhS − MeOH).

Attempted Alkylation of (**9c**) *with Isobutyl Bromide.*—Replacing methyl iodide by isobutyl bromide in the previous method gave none of the alkylated ester but methyl 2-phenylthiopent-3-enoate (**15c**) (74%).

Methyl 2-Cyclopent-1-enyl-2-phenylthiopropanoate (**16ea**).—Methyl cyclopentylidenephenylthioacetate (**9e**) (298 mg, 1.2 mmol) in dry THF (1 ml) was added dropwise to a stirred solution of potassium t-butoxide (161 mg, 1.44 mmol) in dry THF (25 ml) under nitrogen at −78 °C. After 30 min, TMEDA (167 mg, 0.22 ml, 1.44 mmol) was added, followed by methyl iodide (204 mg, 0.09 ml, 1.44 mmol); the cooling bath was then removed. After 1 h the mixture was diluted with ether (25 ml), washed with water (2 × 10 ml) and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (50 g) eluting with light petroleum (b.p. 30—40 °C) to give the *ester* (261 mg, 83%) as an oil, $R_F(CH_2Cl_2)$ 0.61; $\nu_{max.}$(liq.) 1 715 cm^{-1} (CO_2Me); $\delta_H(CDCl_3)$ 7.2—7.5 (5 H, m, PhS), 5.56 (1 H, t, *J* 2 Hz, CH=C), 3.72 (3 H, s, MeO), 2.2—2.6 (4 H, m, CH_2CH=CCH_2), 1.87 (2 H, tt, *J* 7, 7 Hz, CH_2CH_2C=C), and 1.54 (3 H, s, PhSC*Me*) (Found: M^+, 262.1031. $C_{15}H_{18}O_2S$ requires *M*, 262.1027); *m/z* 262 (15%, M^+), 230 (22, *M* − MeOH), 253 (100, *M* − PhS), 252 (33, *M* − PhSH), 121 (20, *M* − PhS − MeOH), 110 (41, PhSH), 93 (44, *M* − PhSH − CO_2Me), and 77 (20, Ph). (This compound was also prepared without using TMEDA in 68% yield, and in 73% yield when conducted at −20 °C).

Ethyl 2-Acetyl-2-phenylthiobut-3-enoate (**20aa**).—Ethyl 2-phenylthiobut-2-enoate (**9a**) (2.56 g, 11.9 mmol) in dry THF (1 ml) was added dropwise to a stirred solution of potassium t-butoxide (1.60 g, 14.3 mmol) in dry THF (100 ml) under nitrogen at −78 °C. After 15 min, acetic anhydride (1.46 g, 1.35 ml, 14.3 mmol) in dry THF (2 ml) was added and the cooling bath removed. After 1 h the mixture was poured into water (100 ml) and extracted with ether (3 × 100 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate (3 × 10 ml), water (2 × 50 ml), and brine (2 × 50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (200 g) eluting with 5% ether in light petroleum (b.p. 30—40 °C) to give the *keto ester* (1.81 g, 58%) as an oil, $R_F(CH_2Cl_2)$ 0.48; $\nu_{max.}$(liq.) 1 740 (CO_2Et), 1 720 (COMe), 1 640 (C=C), 1 590, 1 580, and 1 480 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.2—7.5 (5 H, m, PhS), 6.24 (1 H, dd, *J* 18, 10 Hz, H_2C=C*H*), 5.39 (1 H, d, *J* 10 Hz, H_cH_tC=CH), 5.38 (1 H, d, *J* 18 Hz, H_cH_tC=CH), 4.13 (2 H, q, *J* 7 Hz, OCH_2), 2.20 (3 H, s, COMe), and 1.13 (3 H, t, *J* 7 Hz, *Me*CH_2O) (Found: M^+, 264.0818. $C_{14}H_{16}O_3S$ requires *M*, 264.0820), *m/z* 264 (13%, M^+), 222 (85, *M* − C_2H_2O), 218 (10, *M* − EtOH), 176 (60, *M* − MeCO − EtO), 149 (65, $PHSC_3H_4$), 147 (75, *M* − CO_2Et − EtOH), 110 (90, PhSH), and 109 (100, PhS). Also prepared by the same method were the following.

Ethyl 2-benzoyl-2-phenylthiobut-3-enoate (**20ab**). Ethyl 2-phenylthiobut-2-enoate (**9a**) gave the *keto ester* (76%) as an oil, $R_F(CH_2Cl_2)$ 0.56; $\nu_{max.}$(liq.) 1 740 (CO_2Me), 1 695 (COPh), 1 600, and 1 585 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.8—8.0 and 7.2—7.6 (10 H, m, PhS and PhCO), 6.46 (1 H, dd, *J* 12, 18 Hz, H_2C=C*H*), 5.24 (1 H, d, *J* 12 Hz, H_cH_tC=CH), 5.18 (1 H, d, *J* 18 Hz, H_cH_tC=CH), 3.87 (2 H, q, *J* 7 Hz, CH_2O), and 1.77 (3 H, t, *J* 7 Hz, *Me*CH_2O) (Found: M^+, 326.0954. $C_{19}H_{18}O_3S$ requires *M*, 326.0977); *m/z* 326 (60%, M^+), 280 (8, *M* − EtOH), 253 (8, *M* − CO_2Et), 222 (10, *M* − C_6H_4CO), 217 (35, *M* − PhS), 176 (25, *M* − PhCO − EtO), and 171 (100, *M* − PhS − EtOH).

Methyl 2-cyclopent-1-enyl-3-oxo-2-phenylthiobutanoate (**20ea**). Methyl cyclopentylidenephenylthioacetate (**9e**) gave the *keto ester* (55%) *as an oil*, $R_F(CH_2Cl_2)$ 0.55; $\nu_{max.}$(liq.) 1 750 (CO_2Me), 1 720 (COMe), 1 590, and 1 580 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.3—7.5 (5 H, m, PhS), 6.06 (1 H, t, *J* 2 Hz, C=CH), 3.73 (3 H, s, MeO), 2.2—2.5 (4 H, m, CH_2C=CHCH_2), 2.24 (3 H, s, MeCO), and 1.7—2.0 (2 H, m, CH_2CH_2C=C) (Found: M^+, 290.0981. $C_{16}H_{18}O_3S$ requires *M*, 290.0977); *m/z* 290 (9%, M^+), 258 (43, *M* − MeOH), 248 (75, *M* − C_2H_2O), 247 (38, *M* − MeCO), 231 (5, *M* − CO_2Me), 216 (100, *M* −

MeO − MeCO), 187 (64, *M* − MeCO − HCO_2Me), 181 (22, *M* − PhS), 149 (77, *M* − PhS − MeOH), 121 (54, *M* − PhS − CO_2Me), 110 (39, PhSH), 109 (33, PhS), 107 (47, *M* − PhS − MeO − MeCO), and 77 (41, Ph).

Methyl 2-cyclopent-1-enyl-3-oxo-3-phenyl-2-phenylthiopropenoate (**20eb**). Methyl cyclopentylidenephenylthioacetate (**20ea**) gave the *keto ester* (74%) as prisms, m.p. 83—87 °C, $R_F(CH_2Cl_2)$ 0.65; $\nu_{max.}(CDCl_3)$ 1 740 (CO_2Me), 1 695 (COPh), 1 600, and 1 585 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.9—8.1 and 7.3—7.6 (10 H, m, PhS and PhCO), 6.08 (1 H, t, *J* 2 Hz, C=CH), 3.57 (3 H, s, MeO), and 1.6—2.8 (6 H, m, $CH_2CH_2CH_2$) (Found: M^+, 352.1123. $C_{21}H_{20}O_3S$ requires *M*, 352.1133); *m/z* 352 (9%, M^+), 320 (53, *M* − MeOH), 247 (32, *M* − PhCO), 243 (15, *M* − PhS), 211 (28, *M* − PhS − MeOH), 187 (19, *M* − PhCO − HCO_2Me), 110 (113, PhSH), 105 (100, PhCO), and 77 (30, Ph). Also prepared by a similar method, at −20 °C instead of −78 °C were the following.

E-*Methyl 2-acetyl-2-phenylthiopent-3-enoate* (**20ca**). Methyl 2-phenylthiopent-2-enoate (**9c**) gave the *keto ester* (61%) as an oil, $R_F(CH_2Cl_2)$ 0.50; $\nu_{max.}$(liq.) 1 740 (CO_2Me), 1 725 (COMe), 1 590 (Ph), and 970 cm^{-1} (*trans*-HC=CH); $\delta_H(CDCl_3$, 250 MHz) 7.22—7.43 (5 H, m, PhS), 5.75—5.91 (2 H, m, CH=CH), 3.69 (3 H, s, MeO), 2.22 (3 H, s, MeCO), and 1.74 (3 H, d, *J* 5 Hz, *Me*CH=CH); $\delta_C(CDCl_3)$ 197.6 (s, *C*OMe), 168.7 (s, CO_2Me), 136.2* (d), 135.5 (s), 131.9 (d), 129.4 (d), 128.6* (d), 125.3 (d) (aromatic and olefinic carbons), 71.3 (s, quaternary C), 52.9 (q, CO_2Me), 26.8 (q, *Me*CO), and 18.2 (q, *Me*C=C) (Found: M^+, 264.0834. $C_{14}H_{16}O_3S$ requires *M*, 264.0820); *m/z* 264 (12%, M^+), 222 (100, *M* − C_2H_2O), 190 (79, *M* − MeCO − MeO), and 61 (35).

E-*Methyl 2-benzoyl-2-phenylthiopent-3-enoate* (**20cb**). Methyl 2-phenylthiopent-2-enoate (**9c**) gave the *keto ester* (74%) as prisms, m.p. 98—100 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 69.6; H, 5.50; S, 9.8. $C_{19}H_{18}O_3S$ requires C, 69.9; H, 5.55; S, 9.8%); $R_F(CH_2Cl_2)$ 0.65; $\nu_{max.}(CDCl_3)$ 1 720 (CO_2Me), 1 690 (COPh), 1 600, 1 585 (Ph), and 970 cm^{-1} (*trans*-HC=CH); $\delta_H(CDCl_3)$ 7.8—8.0 and 7.2—7.6 (10 H, m, PhS and PhCO), 6.21 (1 H, dq, *J* 16, 1.5 Hz, MeCH=C*H*), 5.66 (1 H, dq, *J* 16, 6.5 Hz, MeC*H*=CH), 3.4 (3 H, s, MeO), and 1.63 (3 H, dd, *J* 6.5, 1.5 Hz, *Me*CH=CH); $\delta_C(CDCl_3)$ 190.8 (s, *C*OPh), 169.5 (s, CO_2Me), 137.3* (d), 134.8 (s), 132.8 (d), 131.7 (d), 130.6 (s), 129.6 (d), 129.3* (d), 128.5* (d), 128.4* (d), 126.7 (d) (aromatic and olefinic carbons), 69.6 (s, quaternary C), 52.7 (q, CO_2Me), and 18.3 (q, *Me*C=C); *m/z* 326 (4%, M^+), 220 (1, *M* − PhCO), 217 (12, *M* − PhS), 190 (4, *M* − PhCO − MeO), 185 (40, *M* − PhS − MeOH), 110 (20, PhSH), 105 (100, PhCO), and 77 (30, Ph).

[1,3] *Phenylthio Shift Experiments on the Esters* (**16**) *and* (**20**).—*Ethyl 2-benzyl-4-phenylthiobut-2-enoate* (**27ab**). Ethyl 2-benzyl-2-phenylthiobut-3-enoate (**16ab**) (1.03 g, 3.3 mmol), AIBN (500 mg, *ca.* 1 equiv.), and thiophenol (0.3 ml, *ca.* 1 equiv.) were heated in C_6D_6 to 65 °C under nitrogen. The reaction was monitored periodically by cooling the solution and recording its n.m.r. spectrum. No starting ester remained after 2 h. The cooled solution was diluted with ether (50 ml), washed with dilute (*ca.* 0.1M) aqueous sodium hydroxide (3 × 10 ml), water (2 × 10 ml), and brine (2 × 10 ml), and dried ($MgSO_4$). Solvent removal under reduced pressure and column chromatography, eluting with light petroleum (b.p. 30—40 °C)–ether, gave the *ester* (0.961 g, 94%) as a mixture of geometrical isomers, *Z*:*E ca.* 15:85, R_F 0.32 (*Z*), 0.26 (*E*); $\nu_{max.}$(film) 1 715 (C=O), and 1 645 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 7.1—7.5 (10 H, m, Ph and PhS), 6.98 (*E*) and 5.99 (*Z*) (1 H, t, *J* 8 Hz, PhSCH$_2$C*H*=C), 4.15 (*E*) and 4.09 (*Z*) (2 H, q, *J* 7 Hz, O*CH*$_2$Me), 3.69 (*E*) and 4.1 (*Z*) (2 H, d, *J* 8 Hz, PhSC*H*$_2$CH=C), 3.57 (2 H, br s, PhC*H*$_2$) and 1.19 (*E*) and 1.17 (*Z*) (3 H, t, *J* Hz, OCH$_2$*Me*) (Found: M^+, 312.1183. $C_{19}H_{20}O_2S$ requires *M*, 312.1176); *m/z* 312 (30%), 203 (70, *M* − PhS), 202 (60, *M* − H, PhS), 129 (100, *M* − PhS, H, CO_2Et), 110 (40, $PhSH^+$), and 109 (25, PhS^+). Also prepared in a similar way were the following.

Methyl 2,3-dimethyl-4-phenylthiobut-2-enoate (**27ba**). The *ester* (96%) was a mixture of geometrical isomers, *Z*:*E ca.* 3:4 R_F(A) 0.34; $\nu_{max.}$(film) 1 710 (C=O) and 1 630 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 7.1—7.4 (5 H, m, PhS), 3.96 (*Z*) and 3.55 (*E*) (2 H, s, PhSC*H*$_2$) 3.70 (*E*) and 3.58 (*Z*) (3 H, s, CO_2Me), 2.05 (*E*) (3 H, q, *J* 1.5 Hz, *Me*C=CCO$_2$Me), 1.88 and 1.82 (*Z*) (2 × 3 H, each s, *Me*C=C*Me*) and 1.66 (*E*) (3 H, q, *J* 1.5 Hz, C=C*Me*CO$_2$Me) (Found: M^+, 236.0871. $C_{13}H_{16}O_2S$ requires *M*, 236.0868); *m/z* 236 (35%), 127 (100, *M* − PhS), 110 (80, $PhSH^+$), and 109 (45, PhS^+).

Methyl 2-ethyl-4-phenylthiohex-2-enoate (**27db**). The *ester* (92%) was a mixture of geometrical isomers *Z*:*E*, 18:82, which was separated by h.p.l.c. eluting with light petroleum (b.p. 30—40 °C) containing 3% ether, solvent E. The (*E*)-ester (75%) was an oil, R_F (solvent E) 0.19; $\nu_{max.}$(liq.) 1 720 (C=O) and 1 640 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 6.50 (1 H, d, *J* 11.5 Hz, PhSCHC*H*=C), 3.73 (1 H, ddd, *J* 11.5, 8, 6 Hz, PhSC*H*CH=C), 3.67 (3 H, s, CO_2Me), 1.97 (2 H, q, *J* 7.5 Hz, C=CCH$_2$), 1.4—1.9 (2 H, m, PhSCHC*H*$_2$Me), and 0.72 and 0.95 (2 × 3 H, each t, *J* 7.5 Hz, both CH$_2$*Me*). The (*Z*)-*ester* (17%) was an oil, R_F(E) 0.21; $\nu_{max.}$(liq.) 1 715 (C=O) and 1 640 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 7.1—7.4 (5 H, m, PhS), 5.63 (1 H, d, *J* 10.5 Hz, PhSCHC*H*=C), 4.64 (1 H, ddd, *J* 10.5 7.5, 6 Hz, PhSC*H*CH=C), 3.52 (3 H, s, CO_2Me), 2.15 (2 H, q, *J* 7.5 Hz, C=CC*H*$_2$Me), 1.5—1.9 (2 H, m, PhSCHC*H*$_2^*$Me), and 0.88 and 0.97 (2 × 3 H, each t, *J* 7.5 Hz, both CH$_2$*Me*) [Found: (for the mixture) M^+, 264.1184. $C_{15}H_{20}O_2S$ requires *M*, 264.1185]; *m/z* 264 (35%) 155 (100, *M* − PhS), 125 (35, *M* − PhS, H, OMe), 110 (45, $PhSH^+$), and 109 (40, PhS^+).

Repeating the method described above, on 80—100 mg of the esters (below), in a sealed n.m.r. spectroscopy tube gave the following results.

Ethyl 4-phenylthiobut-2-enoate (**28a**). The crude ester (**15a**) containing *ca.* 20% of its isomer (**9a**) gave the ester quantitatively, still containing the impurity, $\delta_H(C_6H_6)$ 6.7—7.2 (5 H, m, PhS), 6.79 (1 H, *J* 16, 7 Hz, PhSCH$_2$C*H*=CH), 5.65 (1 H, d, *J* 16 Hz, PhSCH$_2$CH=C*H*), 3.86 (2 H, q, *J* 7 Hz, O*CH*$_2$Me), 3.12 (2 H, d, *J* 7 Hz, PhSC*H*$_2$CH=CH), and 1.99 (3 H, q, *J* 7 Hz, OCH$_2$*Me*).

Methyl 3-methyl-4-phenylthiobut-2-enoate (**28b**). Similarly the crude ester (**15b**) gave the ester (**28b**) (*Z*:*E*, 2:3) $\delta_H(C_6D_6)$, 6.6—7.5 (5 H, m, PhS), 5.52 (1 H, br d, *J ca.* 3 Hz, CH=C), 4.06 (*Z*) and 3.09 (*E*) (2 H, s, PhSC*H*$_2$), 3.27 (3 H, s, CO_2Me), and 2.19 (*E*) and 1.63 (*Z*) (3 H, s, MeC=C).

Ethyl 2-methyl-4-phenylthiobut-2-enoate (**27aa**). The ester had $\delta_H(C_6D_6)$ (*E* isomer only) 6.8—7.1 (6 H, m, PhS, CH=C), 3.94 (2 H, q, *J* 7 Hz, O*CH*$_2$Me), 3.24 (2 H, d, *J* 8 Hz, PhSC*H*$_2$CH=C), 1.56 (3 H, d, *J* 0.5 Hz, *Me*C=CH), and 0.95 (3 H, t, *J* 7 Hz, OCH$_2$*Me*.

Ethyl 4-phenylthio-2-prop-2-enylbut-2-enoate (**27ac**). The ester had $\delta_H(C_6D_6)$ (6 H, m, PhS, CH=C), 4.8—6.2 (3 H, br m, CH$_2$C*H*=C*H*$_2$), 3.99 (2 H, q, *J* 7 Hz, O*CH*$_2$Me), 3.29 (2 H, d, *J* 8 Hz, PhSC*H*$_2$CH), 3.08 (2 H, br d, *J ca.* 7 Hz, C*H*$_2$CH=CH$_2$), and 1.02 (3 H, t, *J* 7 Hz, OCH$_2$*Me*).

Methyl 2-methyl-4-phenylthiohex-2-enoate (**27da**). The reaction took several hours before complete loss of starting material, and gave predominantly the *E*-isomer of the ester, $\delta_H(C_6H_6)$, 6.8—7.4 (5 H, m, PhS), 6.80 (1 H, dq, *J* 11.5, 1.5 Hz, PhSCHC*H*=CMe), 3.68 (1 H, ddd, *J* 11.5, 8, 6 Hz, PhSC*H*CH=C), 3.39 (3 H, CO_2Me), 1.8—1.5 (2 H, m, PhSCHC*H*$_2^*$Me), 1.44 (3 H, d, *J* 1.5 Hz, CH=C*Me*), and 0.37 (3 H, t, *J* 7 Hz, CH$_2$*Me*).

Methyl 2-benzyl-3-methyl-4-phenylthiobut-2-enoate (**27bc**). A mixture of geometrical isomers of the ester (*Z*:*E*, 1:2) had $\delta_H(C_6D_6)$ (10 H, m, Ph and PhS), 3.70 (*Z*) and 3.52 (*E*) (2 H, s,

PhSCH_2), 3.33 (*Z*) and 3.22 (*E*) (3 H, s, CO_2Me), 3.16 (2 H, s, PhCH_2), and 2.18 (*E*) and 1.72 (*Z*) (3 H, s, C=CMe).

Methyl 2-(2-*Phenylthiocyclopentylidene*)*propanoate* (**27ea**).—The ester (**16ea**) (223 mg, 0.85 mmol), AIBN (140 mg, 0.85 mmol), and thiophenol (94 mg, 0.09 ml, 0.85 mmol) in carbon tetrachloride (0.5 ml) were heated at 70 °C for 5 h. The cooled solution was diluted with ether (10 ml), washed with aqueous sodium hydroxide (5 ml), water (2 × 5 ml), and brine (2 × 5 ml), and dried ($MgSO_4$). Evaporation under reduced pressure gave a mixture of *E* and *Z* isomers of the *ester* (223 mg, 100%) as an oil, R_F(CH_2Cl_2) 0.40—0.49, $\nu_{max.}$(liq.) 1 705 (CO_2Me), 1 640 (C=C), and 1 580 cm^{-1} (Ph); δ_H($CDCl_3$) 7.2—7.6 (5 H, m, PhS), 5.21 and 4.36 (1 H, total, each a broad singlet, PhSC*H*C=C), 3.72 and 3.63 (3 H, total, each a singlet, MeO), and 1.5—2.0 [9 H, m, C=C*Me* and (CH_2)$_3$CHSPh] (Found: M^+, 262.1017. $C_{15}H_{18}O_2S$ requires *M*, 262.1027); *m/z* 262 (21%, M^+), 230 (22, *M* − MeOH), 203 (2, *M* − CO_2Me), 153 (100, *M* − PhS), 121 (20, *M* − PhS − MeOH), 110 (80, PhSH), and 109 (32, PhS).

Ethyl 2-*Benzoyl*-4-*phenylthiobut*-2-*enoate* (**21ab**).—The ester (**20ab**) (289 mg, 0.88 mmol) in dichloromethane (50 ml) containing thiophenol (1 drop) was left in sunlight for 4 weeks. Evaporation under reduced pressure and purification by t.l.c., eluting with dichloromethane, gave a mixture of *E* and *Z* isomers of the *ester* [70 mg, 24% (40% based on recovered starting material)] as an oil, R_F(CH_2Cl_2) 0.36; δ_H($CDCl_3$) 7.1—8.0 (10 H, m, PhS and PhCO), 6.59 (1 H, t, *J* 8 Hz, C=CH), 4.14 (2 H, q, *J* 7 Hz, CH_2O), 3.61 (2 H, d, *J* 8 Hz, PhSCH_2), and 1.07 (3 H, t, *J* 7 Hz, *Me*CH_2O).

Methyl 2-*Benzoyl*-4-*phenylthiopent*-2-*enoate* (**21cb**).—The ester (**20cb**) (170 mg, 0.52 mmol), AIBN (40 mg, 0.24 mmol), and thiophenol (110 mg, 0.1 ml, 1.0 mmol) in carbon tetrachloride (5 ml) were refluxed for 24 h. The cooled solution was diluted with ether (20 ml), washed with sodium hydroxide (10 ml), water (2 × 10 ml), and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (50 g) eluting with 5% ether in light petroleum (b.p. 30—40 °C) to give a mixture of *E* and *Z* isomers of the *ester* (96 mg, 56%) as an oil, R_F(CH_2Cl_2) 0.42; $\nu_{max.}$(liq.) 1 720 (CO_2Me), 1 665 (COPh), 1 630 (C=C), 1 595, and 1 580 cm^{-1} (Ph); δ_H($CDCl_3$) isomer A: 7.2—7.7 (10 H, m, PhS and PhCO), 7.09 (1 H, d, *J* 12 Hz, C=CH), 3.88 (1 H, dq, *J* 12, 6 Hz, PhSC*H*Me), 3.65 (3 H, s, MeO), and 1.43 (3 H, d, *J* 6 Hz, PhSCH*Me*); and isomer B: 7.2—7.7 (10 H, m, PhS and PhCO), 6.34 (1 H, d, *J* 11 Hz, C=CH), 5.01 (1 H, dq, *J* 11, 7 Hz, PhSC*H*Me), 3.55 (3 H, s, MeO), and 1.42 (3 H, d, *J* 7 Hz, PhSCH*Me*) (Found: M^+, 326.0977. $C_{19}H_{18}O_3S$ requires *M*, 326.0977); *m/z* 326 (10%, M^+), 217 (24, *M* − PhS), 185 (100, *M* − PhS − MeOH), 158 (10, *M* − PhS − CO_2Me), 110 (30, PhSH), 109 (12, PhS), 105 (94, PhCO), and 77 (51, Ph). [This rearranged ester was also obtained in 15% yield (30% based on recovered starting material) after 7 h refluxing of ester (**20cb**) with 2 equiv. of tosic acid in benzene.] Also prepared in the same way was the following.

Methyl 3-*oxo*-2-(2-*phenylthiocyclopentylidene*)*butanoate* (**21ea**). Ester (**20ea**) gave a mixture of *E* and *Z* isomers of the rearranged ester (53%) as an oil, R_F(CH_2Cl_2) 0.31, $\nu_{max.}$(liq.) 1 725 (CO_2Me), 1 695 (COMe), 1 600, and 1 590 cm^{-1} (Ph); δ_H($CDCl_3$) 7.3—7.8 (5 H, m, PhS), 4.97 and 4.31 (1 H total, m, PhSC*H*), 3.68 (3 H, s, MeO), 2.97 (3 H, s, COMe), and 1.2—2.0 [6 H, m, (CH_2)$_3$] (Found: M^+, 290.0963. $C_{16}H_{18}O_3$ requires *M*, 290.0977); *m/z* 290 (7%, M^+), 258 (5, *M* − MeOH), 181 (24, *M* − PhS), 149 (64, *M* − PhS − MeOH), 139 (24, *M* − PhSH − MeCO), 121 (12, *M* − PhSH − CO_2Me), 110 (100, PhSH), and 109 (30, PhS).

Methyl 2-*Benzoyl*-4-*phenylsulphinyloxypent*-2-*enoate* (**31**).—MCPBA (1.0 g, 5.5 mmol) in dichloromethane (20 ml) was added to a stirred solution of the ester (**20cb**) (630 mg, 1.93 mmol) in dichloromethane under nitrogen at 0 °C. After 20 min the mixture was poured into 10% aqueous sodium sulphite (20 ml) and extracted with dichloromethane (2 × 20 ml); the extract was dried ($MgSO_4$) and evaporated under reduced pressure to give the *sulphinate ester* (691 mg, 100%) as a roughly equal mixture of four isomers, some of which crystallised slowly at −20 °C to give a slushy solid, R_F(CH_2Cl_2) 0.09, (Et_2O) 0.68; $\nu_{max.}$(liq.) 1 725 (CO_2Me), 1 675 (COPh), 1 600, and 1 580 cm^{-1} (Ph); δ_H($CDCl_3$, 250 MHz) 7.83—7.92, 7.67—7.76, and 7.33—7.61 (10 H, m, PhS and PhCO), 7.11, 7.02, 6.51, and 6.34 (1 H total, each a doublet, *J* 8 Hz, C=CH), 5.88, 5.68, 4.95, and 4.80 (1 H, total, each a dq, *J* 8, 6.5 Hz, C=CHC*H*), 3.69, 3.64, and 3.63 (3 H total, each a singlet, MeO), 1.52, 1.47, 1.39, and 1.31 (3 H total, each a doublet, *J* 6.5 Hz, *Me*CH); *m/z* 233 (0.4%, *M* − PhSO), 217 (100, *M* − $PhSO_2$), 1.85 (50, *M* − $PhSO_2$ − MeOH), 158 (19, *M* − $PhSO_2$ − CO_2Me), 125 (24, PhSO), 105 (87, PhCO), and 77 (62, Ph).

Attempted Hydrolysis of Sulphinate Ester (**31**).—A 0.1M-phosphate buffer of pH 7 was prepared by adding 1.0M-hydrochloric acid (5 ml) to 0.4M-di-sodium hydrogen orthophosphate (25 ml) and making the solution up to 100 ml with distilled water. A portion of this buffer solution (15 ml) was added to a stirred solution of the ester (**31**) (356 mg, 0.99 mmol) in methanol (15 ml) under nitrogen at 60 °C. After 30 min the cooled mixture was concentrated under reduced pressure and extracted with ether (4 × 20 ml). The combined extracts were washed with water (2 × 10 ml) and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (50 g) eluting with 5% ether in light petroleum (b.p. 30—40 °C to give *methyl* 2-*benzoyl*-4-*oxopent*-2-*enoate* (37 mg, 16%) as an oil, R_F(CH_2Cl_2) 0.55; $\nu_{max.}$(liq.) 1 715 cm^{-1} (C=O); δ_H($CDCl_3$) 7.9—8.1 and 7.4—8.6 (5 H, m, PhCO), 6.46 (1 H, br s, CH=C), 3.83 (3 H, s, MeO), and 2.34 (3 H, s, MeCO); *m/z* 216 (90, *M* − CH_4), 185 (100, *M* − MeOH − Me), 105 (37, PhCO), and 77 (33, Ph); and methyl phenylsulphinate[63] (73.8 mg, 48%) as an oil, R_F(CH_2Cl_2) 0.30.

Butyl 4-*Phenylthiopent*-3-*enoate* (**37b**).—Butyl 4-phenylthiopent-2-enoate (**34**) (260 mg, 1 mmol) was added to a stirred, cooled (−78 °C) solution of potassium t-butoxide (126 mg, 1.1 mmol) in dry THF (5 ml) under nitrogen. After 0.5 h the solution was quickly poured into aqueous sodium hydrogen carbonate (25 ml), extracted into ether (3 × 10 ml), and the organic extracts washed with brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The product was purified by p.l.c. to give the *ester* (95%) as a mixture of geometrical isomers, M and N, R_F(B) 0.54; $\nu_{max.}$(liq.) 1 740 (C=O) and 1 630 cm^{-1} (C=C); δ_H($CDCl_3$) 7.1—7.5 (5 H, m, PhS), 5.76—6.96 (1 H, m, MeC=C*H*), 4.10 (2 H, t, *J* 6.5 Hz, OCH_2), 3.40 (N) and 3.14 (M) (2 H, q, *J* 8 Hz, C=CHCH_2CO_2), 1.93 (N) and 1.91 (M) (3 H, br s, *Me*C=CH), 1.1—1.8 (4 H, m, $OCH_2CH_2CH_2$Me), and 0.94 (3 H, t, *J* 6.5 Hz, CH_2*Me*) (Found: M^+, 264.1191. $C_{15}H_{20}O_2S$ requires *M*, 264.1184); *m/z* 264 (75%), 163 (100, *M* − CO_2Bu), and 148 (50, *M* − MeCO_2Bu). Also prepared in this way was the following.

Ethyl 4-*phenylthiobut*-3-*enoate* (**37a**). The ester (**33**) gave the *ester* (89%) as an oily mixture of isomers M and N, R_F(B) 0.62 (M) and 0.58 (N); $\nu_{max.}$(film) 1 725 (C=O) and 1 630 cm^{-1} (C=C); δ_H($CDCl_3$) 7.1—7.6 (5 H, m, PhS), 6.29—6.45 (1 H, m, CH=C*H*SPh), 5.78—6.20 (1 H, m, C*H*=CHSPh), 4.14 (M) and

4.12 (N) (2 H, q, *J* 7 Hz, OCH_2Me), 6.27 (M) (2 H, dd, *J* 7, 1.5 Hz, CH_2CO_2Et), 3.12 (N) (2 H, dd, *J* 7, 0.5 Hz, CH_2CO_2Et), and 1.23 (M) and 1.22 (N) (3 H, t, *J* 7 Hz, OCH_2Me) (Found: M^+, 222.0715. $C_{12}H_{14}O_2S$ requires *M*, 222.0715); *m/z* 222 (70%), 193 (25, *M* − Et), 176 (30, *M* − H, OEt), 149 (100, *M* − CO_2Et), 110 (45, $PhSH^+$), and 109 (75, PhS^+).

Butyl 2-Methyl-4-phenylthiopent-3-enoate (**38a**).—Butyl 4-(phenylthio)pent-2-enoate (**34**) (130 mg, 0.5 mmol) in dry THF (1 ml) was added slowly to a stirred, cooled (−78 °C) solution of potassium t-butoxide (60 mg, 0.5 mmol) in dry THF (2 ml) under a nitrogen atmosphere. After 0.5 h, methyl iodide (0.2 g, excess) in dry THF (1 ml) was added rapidly and the mixture stirred at room temperature for 3 h; it was then diluted with ether (25 ml). The suspension was washed with water (2 × 10 ml) and brine (2 × 10 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure. N.m.r. spectroscopy showed the product to contain a little of the starting ester (*ca.* 5%), and the dimethylated ester (**39**; R^2 = Me, *ca.* 10%) as well as the ester (**38a**). P.l.c. gave the ester (84%) as a mixture of isomers, as an oil, R_F(B) 0.58, see below.

Butyl 2-Methyl-4-phenylthiopent-3-enoate (**38a**).—Under nitrogen at −78 °C, BuLi (1.5M solution in hexane; 0.4 ml) was added to dry di-isopropylamine (0.3 ml) in dry THF (10 ml), followed after 0.5 h by dry TMEDA (0.1 ml) and the ester (**34**) (0.16 g). The orange–yellow anion solution was stirred for 0.5 h, methyl iodide (0.1 ml, excess) added, stirring continued for 1 h and the mixture allowed to warm to room temperature. Aqueous ammonium chloride was added, the THF layer 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* (0.14 g, 83%), a single geometric isomer, R_F 0.60; $\nu_{max.}$(liq.) 1 730 (C=O) and 1 625 cm^{-1} (C=CS); $\delta_H(CDCl_3)$ 7.1—7.4 (5 H, m, Ph), 5.74 (1 H, dq, *J* 9.5, 1.5 Hz, MeC=C*H*CH), 4.09 (2 H, t, *J* 6 Hz, $CO_2CH_2CH_2$), 3.39 (1 H, dq, *J* 9.5, 1.5 Hz, MeC=CHCH), 1.91 (3 H, d, *J* 1.5 Hz, *Me*C=CH), 1.8—1.2 (4 H, m, CH_2), 1.25 (3 H, d, *J* 7 Hz, *Me*CH), and 0.94 (3 H, t, *J* 6.5 Hz, $MeCH_2$); *m/z* 278 (M^+, 20%), 177 (100), 149 (13), and 113 (27) (Found: C, 69.1; H, 8.2; S, 11.2. $C_{16}H_{22}O_2S$ requires C, 69.0; H, 8.0; S, 11.5%). Repetition of the reaction replacing the TMEDA with HMPA (0.2 ml) (the anion colour was dark red) gave (**38a**) in 77% yield after preparative t.l.c. In the absence of a co-solvent a mixture of monomethylated products (M^+ 278 only), R_F 0.50—0.60, was formed (70% after preparative t.l.c.), containing *ca.* 50% of (**38a**) by n.m.r.

Alkylation of the Ester (**35**) *with Methyl Iodide*.—Under nitrogen at −78 °C, BuLi (1.5M solution in hexane; 0.5 ml) was added to dry di-isopropylamine (0.3 ml) in dry THF (20 ml), followed after 0.5 h by dry HMPA (0.2 ml) and the ester (0.19 g). After 0.5 h, methyl iodide (0.1 ml) was added to the lemon coloured anion, stirring continued for 2 h, and the mixture worked up as above. Preparative t.l.c. gave 0.16 g of a mixture (3:3:2) of (**41**), (**42**), and (**43**), R_F 0.6, *m/z* (M^+) 292 and 278. The n.m.r. spectrum in $CDCl_3$ showed peaks for (**41**) at δ 2.01 and 1.94 (MeC=C) and for (**42**) at δ 4.95—5.10 (C=CH_2).

Butyl 2,2-Dimethyl-4-phenylthiopent-3-enoate (**39a**).—Butyl 4-phenylthiopent-2-enoate (**34**) (130 mg, 0.5 mmol) in dry THF (1 ml) was added dropwise to a stirred solution, cooled (−78 °C) solution of potassium t-butoxide (150 mg, 1.3 mmol, 2.6 equiv.) in dry THF (5 ml) under nitrogen. After 0.5 h a solution of methyl iodide (0.5 g, excess) in dry THF (2 ml) was added dropwise with stirring over *ca.* 0.5 h; the mixture was then stirred at room temperature for 4 h. The suspension was diluted with ether (30 ml), washed with water (2 × 10 ml) and brine (2 × 10 ml), and dried ($MgSO_4$). Solvent removal under reduced pressure, followed by p.l.c. gave the *ester* (120 mg, 83%) as a colourless oily mixture of isomers M and N, (M:N, 9:1), R_F(B) 0.61; $\nu_{max.}$(liq.) 1 725 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 5.98 (M) and 5.88 (N), (1 H, m, MeC=C*H*), 3.91—4.21 (2 H, m, OCH_2), 1.91 (N) and 1.83 (M) (3 H, d, *J* 1 Hz, *Me*C=CH), 1.2—1.8 (4 H, m, OCH_2CH_2), 1.39 (6 H, s, CMe_2), and 0.92—1.06 (3 H, m, CH_2Me) (Found: M^+, 291.1521. $C_{17}H_{24}O_2S$ requires *M*, 292.1497), *m/z* 292 (5%), 191 (100, *M* − CO_2Bu), and 110 (40, $PhSH^+$). Also prepared in this way were the following.

Butyl 2,2-diethyl-4-phenylthiopent-3-enoate (**39b**). The *ester* (88%) was an oil, R_F(B) 0.64; $\nu_{max.}$(liq.) 1 725 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.2—7.5 (5 H, m, PhS), 5.79 (1 H, br s, C*H*=Me), 4.0—4.2 (2 H, m, OCH_2CH_2), 1.82 (3 H, d, *J* 1 Hz, CH=C*Me*), and 1.2—2.1 and 0.8—1.1 (17 H, m, other CHs) (Found: M^+, 320.1840. $C_{19}H_{28}O_2S$ requires *M*, 320.1870); *m/z* 320 (5%), 219 (100, *M* − CO_2Bu), and 110 (40, $PhSH^+$).

Butyl 4-phenylthio-2,2-dipropylpent-3-enoate (**39c**). The *ester* (79%) was an oil, R_F(B) 0.69; $\nu_{max.}$ 1 730 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 5.90 (1 H, br s, C*H*CMe), 3.99—4.19 (2 H, m, OCH_2CH_2), 1.0—2.0 (12 H, m, other CH_2s), 1.81 (3 H, d, *J* 1 Hz, CH=C*Me*), and 0.80—1.05 (9 H, m, other Mes) (Found: M^+, 348.2127. $C_{21}H_{32}O_2S$ requires *M*, 348.2131); *m/z* 348 (5%) and 247 (100, *M* − CO_2Bu).

Ethyl 2-Benzyl-2-methyl-4-phenylthiobut-3-enoate (**13b**).—The ester (**27ab**) (125 mg, 0.4 mmol) in dry THF (1M-solution; 0.4 ml) was added dropwise to a stirred, cooled (−78 °C) solution of potassium t-butoxide (67 mg, 0.6 mmol) in dry THF (0.5M-solution; 1.2 ml) under nitrogen. The solution was stirred for 20 min, during which time it darkened from orange to deep red-brown, and was then quenched with methyl iodide (115 mg, 0.8 mmol) in dry THF (2M-solution; 0.4 ml) added slowly. After a further 30 min at −78 °C, the suspension was allowed to attain room temperature slowly (5—6 h). The mixture was diluted with ether (20 ml), washed with aqueous sodium hydrogen carbonate (2 × 5 ml) and brine (2 × 5 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The product was purified by p.l.c. to give the *ester* (118 mg, 91%) as an oil, R_F(A) 0.38 major, 0.35 trace, as a mixture of geometrical isomers shown by n.m.r. spectroscopy to be predominantly one isomer (*ca.* 7:1); $\nu_{max.}$(film) 1 730 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.1—7.6 (10 H, m, Ph and PhS), 6.14 (2 H, s, C*H*=C*H*), 4.13 (2 H, q, *J* 7 Hz, OCH_2Me), and 3.10 and 2.92 (3 H, t, *J* 7 Hz, OCH_2Me) (Found: M^+, 326.1340. $C_{20}H_{22}O_2S$ requires *M*, 326.1342); *m/z* 326 (10%), 235 (100, *M* − $PhCH_2$), and 161 (30, *M* − H, $PhCH_2$, CO_2Et). The following were prepared in a similar way.

Ethyl 2-benzyl-2-ethyl-4-phenylthiobut-3-enoate (**38c**). The ester (89%) was an oil, R_F(A) 0.28, $\nu_{max.}$(liq.) 1 730 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.0—7.3 (10 H, m, Ph and PhS), 5.98 and 6.16 (2 H, each d, *J* 16.5 Hz, C*H*=C*H*), 4.14 (2 H, q, *J* 7 Hz, OCH_2Me), 2.97 and 3.12 (2 H, AB quarter, *J* 14 Hz, $PhCH_2$), 1.6—2.0 (2 H, m, CCH_2Me), 1.22 (3 H, q, *J* 7 Hz, OCH_2Me), and 0.91 (3 H, q, *J* 7 Hz, CH_2Me) (Found: M^+, 340.1497. $C_{21}H_{24}O_2S$ requires *M*, 340.1488); *m/z* 340 (10%), 249 (100, *M* − $PhCH_2$), 203 (40, *M* − H, $PhCH_2$, OEt), and 175 (35, *M* − H, $PhCH_2$, CO_2Et).

Methyl 2-ethyl-2-methyl-4-phenylthiohex-3-enoate (**38d**). The *ester* (88%) was an oily mixture of isomers M and N, (M:N, 6:1), R_F(A) 0.40, $\nu_{max.}$(liq.) 1 730 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.1—7.4 (5 H, m, PhS), 5.89 (N) and 5.81 (M) (1 H, br s, CH=C), 3.69 (N) and 3.54 (M) (3 H, s, CO_2Me), 1.6—2.3 (M) (4 H, m, C=CCH_2Me, CH_2Me), 2.09 (N) (2 H, q, *J* 7.5 Hz, C=CCH_2Me), 1.4—1.9 (N) (2 H, m, CCH_2Me), 1.40 (M) and 1.34 (N) (3 H, s, Me), 0.08 (M) and 1.01 (N) (3 H, t, *J* 7.5 Hz, C=CCH_2Me), and 0.95 (M) and 0.86 (N) (3 H, t, *J* 7 Hz, CH_2Me), (Found: M^+,

278.1341. $C_{16}H_{22}O_2S$ requires *M*, 278.1330), *m/z* 278 (20%), 219 (100, *M* − CO_2Me), 169 (70, *M* − PhS), 110 (48, $PhSH^+$), and 109 (45, PhS^+).

Reductive Removal of PhS *from the Keto Ester* (**20aa**).—Lithium shot (21 mg, 3 mmol, washed in hexane) was added to a mixture of liquid ammonia (25 ml) and THF (25 ml) and stirred for 1.5 h. Ester (**21aa**) (377 mg, 1.43 mmol) in THF (1 ml) was added, and after 30 min methyl iodide (852 mg, 0.37 ml, 6 mmol). The mixture was stirred for 5 h as the ammonia evaporated and then diluted with ether (25 ml), washed with water (2 × 20 ml), and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by t.l.c. eluting with dichloromethane to give the ester (**16aa**) (9 mg, 3%) as an oil.

(E)-*Methyl* 2-*Benzoylpent*-3-*enoate* (**44**).—Aluminium turnings (270 mg, 10 mmol) were placed in 2% aqueous mercuric chloride for 15 s, rinsed with ethanol and then ether, and immediately placed in a solution of the ester (**20cb**) (326 mg, 1 mmol) in THF (20 ml) containing water (2 ml). After being stirred for 10 min the mixture was filtered through Celite and the precipitate washed with THF. The filtrate and washings were concentrated under reduced pressure, diluted with ether (20 ml), washed with aqueous sodium hydroxide (10 ml), water (2 × 10 ml), and brine (2 × 10 ml), and dried ($MgSO_4$). Evaporation under reduced pressure and purification by t.l.c. eluting with dichloromethane gave the β-*keto ester* [86 mg, 39%, (42% based on recovered starting material)] as an oil, $R_F(CH_2Cl_2)$ 0.36; $\nu_{max.}$(liq.) 1 735 (CO_2Me), 1 685 (COPh), 1 600, 1 580 (Ph), and 970 cm^{-1} (*trans*-HC=CH); $\delta_H(CDCl_3)$ 8.0—8.2 and 7.4—7.7 (5 H, m, PhCO), 5.6—6.1 (2 H, m, CH=CH), 4.99 (1 H, d, *J* 8 Hz, C*H*COPh), 3.74 (3 H, s, CO_2Me), and 1.74 (3 H, d, *J* 5 Hz, *Me*CH=CH) (Found: M^+, 218.0940. $C_{13}H_{14}O_3$ requires *M*, 218.0943); *m/z* 218 (3%, M^+), 186 (2, *M* − MeOH), 158 (4, *M* − HCO_2Me), 105 (100, PhCO), 77 (45, Ph), and 69 (8).

(E)-*Methyl* 2-(1-*Hydroxybenzyl*)*pent*-3-*enoate* (**45**).—Repetition of the above procedure, but stirring for 5 h instead of 10 min gave the β-*hydroxy ester* (96 mg, 44%) as an oil, $R_F(CH_2Cl_2)$ 0.1—0.2 (Et_2O) 0.72; $\nu_{max.}$(liq.) 3 440br (OH), 1 730 (CO_2Me), and 970 cm^{-1} (*trans*-HC=CH); $\delta_H(CDCl_3)$ 7.33 (5 H, m, Ph), 5.5—5.7 (2 H, m, HC=CH), 4.95 (1 H, d, *J* 7 Hz, PhC*H*OH), 3.55 (3 H, s, MeO), 3.27 (1 H, dd, *J* 7, 7 Hz, C*H*CO_2Me), 2.85 (1 H, br s, OH), and 1.67 (3 H, d, *J* 4.5 Hz, *Me*CH=CH) (Found: M^+, 220.1106. $C_{13}H_{16}O_3$ requires *M*, 220.1099); *m/z* 220 (1%, M^+), 143 (2, *M* − Ph), 114 (100, *M* − PhCHO), 107 (30, PhCHOH), 105, (22, PhCO), 82 (32, *M* − PhCHOH − MeO), and 77 (24, Ph).

Methyl 2-*Benzoyl*-3-*phenylthiopentanoate* (**49**).—The ester (**20cb**) (163 mg, 0.5 mmol) in ethanol (5 ml) was added to a stirred solution of sodium hydroxide (40 mg, 1.0 mmol) and thiophenol (220 mg, 0.2 ml, 2 mmol) in ethanol (20 ml). After 1.5 h the mixture was diluted with ether (50 ml) and brine (20 ml), washed with water (3 × 20 ml) and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (70 g) eluting with 5% ether in light petroleum (b.p. 30—40 °C) to give the *ester* (94 mg, 57%) as an oil, $R_F(CH_2Cl_2)$ 0.53; $\nu_{max.}$(liq.) 1 740 (CO_2Me), 1 680 (COPh), 1 595, and 1 580 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.9—8.1 and 7.2—7.7 (10 H, m, PhS and PhCO), 4.6—4.7 (1 H, m, PhCOC*H*), 3.7—4.0 (1 H, m, PhSC*H*), 3.67 and 3.62 (3 H total, each a singlet, MeO, 2 diastereoisomers), 1.3—1.8 (2 H, m, $MeCH_2$), and 1.07 and 1.00 (3 H total, each a triplet, *J* 6 Hz, $MeCH_2$, 2 diastereoisomers) (Found: M^+, 328.1159. $C_{19}H_{20}O_3S$ requires *M*, 328.1133); *m/z* 328 (49%, M^+), 269 (8, *M* − CO_2Me), 223 (10, *M* − PhCO), 219 (12, *M* − PhS), 218 (38, *M* − PhSH), 191 (35, *M* − PhCO − MeOH), 187 (41, *M* − PhS − MeOH), 186 (68, *M* − PhSH − MeOH), 159 (41, *M* − PhSH − CO_2Me), and 158 (100, *M* − PhSH − HCO_2Me), and *methyl* 2-*benzoylpent*-2-*enoate* (**48**) (23 mg, 21%) as a 1:1 mixture of geometrical isomers, an oil, $R_F(CH_2Cl_2)$ 0.31; $\nu_{max.}$(liq.) 1 720 (CO_2Me), 1 675 (COPh), 1 640 (C=C), 1 600, and 1 580 cm^{-1} (Ph); $\delta_H(CDCl_3$, 250 MHz), isomer A; 7.87—7.91 and 7.44—7.63 (5 H, m, PhCO), 7.16 (1 H, t, *J* 8.0 Hz, C=CH), 3.68 (3 H, s, MeO), 2.10 (2 H, dq, *J* 8.0, 7.5 Hz, $MeCH_2$), and 1.02 (3 H, t, *J* 7.5 Hz, $MeCH_2$); isomer B; 7.87—7.91 and 7.44—7.63 (5 H, m, PhCO), 6.62 (1 H, t, *J* 7.6 Hz, C=CH), 3.70 (3 H, s, MeO), 2.60 (2 H, dq, *J* 7.6, 7.6 Hz, $MeCH_2$), and 1.13 (3 H, t, *J* 7.6 Hz, $MeCH_2$) (Found: M^+, 218.0954. $C_{13}H_{24}O_3$ requires *M*, 218.0943); *m/z* 218 (12%, M^+), 187 (9, *M* − MeO), 186 (17, *M* − MeOH), 159 (7, *M* − CO_2Me), 158 (31, *M* − HCO_2Me), 105 (10, PhCO), and 77 (29, Ph). The same procedure, but using 2 equiv. of sodium hydroxide and 3 equiv. of thiophenol gave the conjugated enone (**48**) (81%) as a 4:1 mixture of isomers A and B, while 1 equiv. of sodium hydroxide and 1 equiv. of thiophenol gave the β-phenylthio ester (**49**) (34%) and the non-conjugated enone (**44**) (16%), after only 15 min.

Ethyl 2-*Acetyl*-3-*phenylthiopentanoate* (**50**).—Repetition of the above procedure using the ester (**20aa**) with 1.3 equiv. of sodium hydroxide and thiophenol, and a reaction of only 5 min gave the *ester* (47%), $R_F(CH_2Cl_2)$ 0.36; $\delta_H(CDCl_3)$ 7.3—7.6 (5 H, m, PhS), 4.22 (2 H, q, *J* 7 Hz, CH_2O), 3.4—3.9 (2 H, m, PhSC*H*C*H*CO_2Et), 2.21 and 2.26 (3 H total, each a singlet, COMe, 2 diastereoisomers), 1.30 (3 H, t, *J* 7 Hz, $MeCH_2O$), and 1.27 and 1.34 (3 H total, each a doublet, *J* 7 Hz, *Me*CH); *m/z* 266 (100%, M^+), 177 (90, *M* − EtOH − MeCO), 157 (50, *M* − PhS), 115 (70, *M* − PhS − C_2H_2O), and 110 (100, PhSH).

(Z)-2-*Phenylthiobut*-2-*enoic Acid* (**46**).—Sodium hydroxide solution (10%; 0.9 ml, 2.25 mmol) was added to a solution of the ester (**20aa**) (160 mg, 0.61 mmol) in methanol (5 ml) under nitrogen. After 2.5 h the mixture was acidified with dilute hydrochloric acid (0.75 ml), diluted with water (20 ml), and extracted with ether (2 × 20 ml); the combined extracts were washed with water (2 × 10 ml) and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by t.l.c. eluting with dichloromethane to give the *acid* (44 mg, 37%) as needles, m.p. 54—89 °C (decomp.) $R_F(CH_2Cl_2)$ 0.05 (Et_2O) 0.41—0.52; $\nu_{max.}(CDCl_3)$ 2 500—3 500 (CO_2H), 1 680 (CO_2H), 1 605, and 1 585 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 10.17 (1 H, br s, CO_2H), 7.73 (1 H, q, *J* 7 Hz, C=CH), 7.25 (5 H, br s, PhS), and 2.10 (3 H, d, *J* 7 Hz, Me) (Found: M^+, 194.0401. $C_{10}H_{10}O_2S$ requires *M*, 194.0401); *m/z* 194 (95%, M^+), 176 (4, *M* − H_2O), 168 (13, *M* − C_2H_2), 149 (85, *M* − CO_2H), 134 (35, *M* − CO_2H − Me), 121 (12), 110 (55, PhSH), 109 (50, PhS), and 59 (100, *M* − PhS − C_2H_2).

Ethyl 2-*Acetylbut*-2-*enoate* (**47**).—Trimethylsilyl chloride (457 mg, 0.5 ml, 3.93 mmol) was added to a solution of anhydrous sodium iodide (589 mg, 3.93 mmol) and the ester (**20aa**) (5.9 mg, 1.97 mmol) in dry acetonitrile (10 ml) under nitrogen and the mixture stirred at 40 °C for 4 h. After cooling, the mixture was diluted with water (25 ml), extracted with ether (3 × 20 ml), the combined extracts were washed with aqueous sodium thiosulphate (2 × 25 ml), water (2 × 25 ml), and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with 5% ether in light petroleum (b.p. 30—40 °C) to give the two isomers of the β-keto ester:* major

* This compound has been prepared previously as a mixture of geometrical isomers, J. Bruhn, H. Heimgarther, and H. Schmid, *Helv. Chim. Acta.*, 1979, **62**, 2630.

isomer (59 mg, 38%), $R_F(CH_2Cl_2)$ 0.178; $\delta_H(CDCl_3)$ 6.89 (1 H, q, *J* 7.5 Hz, C=CH), 4.27 (2 H, q, *J* 7 Hz, CH_2O), 2.31 (3 H, s, MeCO), 1.97 (3 H, d, *J* 7.5 Hz, *Me*CH=C), and 1.33 (3 H, t, *J* 7 Hz, *Me*CH_2O); minor isomer (38 mg, 24%), $R_F(CH_2Cl_2)$ 0.29; $\delta_H(CDCl_3)$ 6.89 (1 H, q, *J* 7 Hz, C=CH), 4.15 (2 H, q, *J* 7 Hz, CH_2O), 2.34 (3 H, s, MeCO), 1.87 (3 H, d, *J* 7 Hz, *Me*CH=C), and 1.28 (3 H, t, *J* 7 Hz, *Me*CH_2O).

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