Synthesis of α-Phenylthio Enones and Esters of α-Phenylthio Alkenoic Acids

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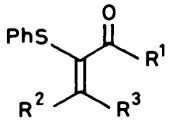
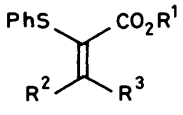
The title compounds can be made by a Pummerer dehydration from the corresponding saturated sulphoxides. The alkylation of anions from saturated and unsaturated ketones is described.

α-Phenylthio enones (**1**) and the related esters (**2**) are in demand as Michael acceptors,[1–6] Diels-Alder dienophiles,[7] and annelating agents.[8] We report the synthesis of examples of these compounds which we have used to make extended enolate anions.[9,10]

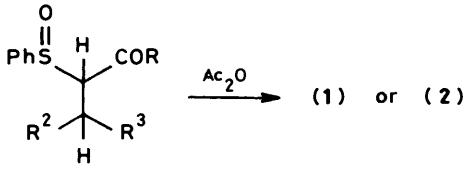


(1)



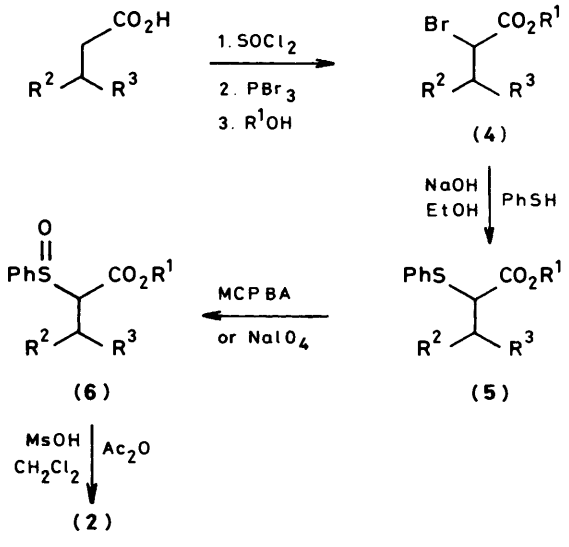
(2)

Compounds of these classes (**1**) and (**2**) have been made by condensation of phenylthio (PhS)-stabilised enolates with aldehydes and ketones,[4,11] from diazo ketones,[12] from phenylthioalkynes,[13] by elimination of water[3,14,15] or HCl[16,17] from, or by direct oxidation[18] of saturated α-phenylthio carbonyl compounds, from the corresponding sulphonium salts,[19] and from the corresponding sulphoxides (**3**) by a Pummerer-style elimination of water.[1,2,20,21] The one-step synthesis of 2-phenylthiocyclopent-2-enone from cyclo-pentanone and PhSCl[22] no doubt involves sulphenylation and a similar Pummerer-style oxidation.[6]



(3)

The unsaturated esters (**2**) were made in a straightforward manner *via* the α-bromo esters (**4**), the saturated α-phenylthio compounds (**5**), and the sulphoxides (**6**). Oxidation of the sulphides (**5**) to the sulphoxides (**6**) was carried out either with an exact equivalent of *meta*-chloroperbenzoic acid (MCPBA) or with a 3- to 5-fold excess of sodium periodate. In the latter case a room temperature evaporation of the methanol solvent allowed extraction of the sulphoxides (**6**) into ether in a state pure enough for the Pummerer elimination. At room temperature, the Pummerer elimination is very slow,[20] but at 40 °C with acetic anhydride and methanesulphonic acid (MsOH) in CH_2Cl_2 the reaction is complete in a few hours without any competing PhSOH elimination. The esters (**2**) are formed (Table 1) as mixtures of geometrical isomers, the *Z*-isomer being the more stable, and they are interconverted on heating, *e.g.*. by distillation, and slowly on standing even in the dark. Separation by chromatography gave the pure *E*- and *Z*-isomers easily distinguished by n.m.r. as the β-vinyl proton occurs at much lower field (*ca.* δ 7.5) in the *Z* isomer than in the *E*-isomer (*ca.* δ 6.5).



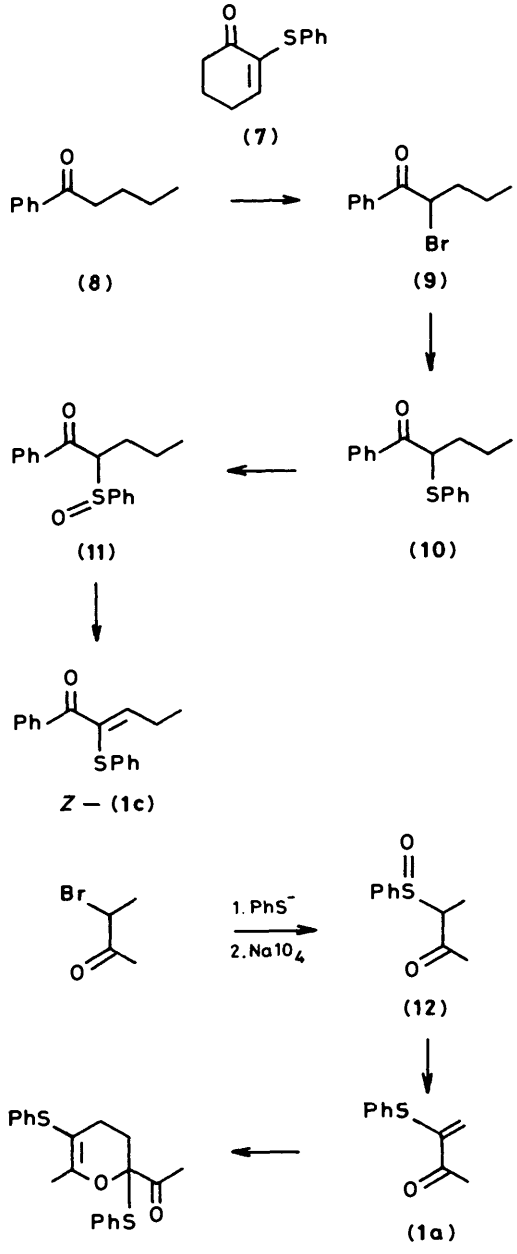
The synthesis of the ketones (**1**) is similarly straightforward if the carbon skeleton is symmetrical or blocked on one side. Thus cyclohexanone gives (**7**)[20] and the phenyl ketone (**8**) gives (**1c**) by the same procedure. We have previously made the ketone

Table 1. Synthesis of esters of α-phenylthioalkenoic acids (**2**)

				Yield of products (%)				δ_H(vinyl)	
Series	R^1	R^2	R^3	(**5**)	(**6**)	(**2**)	*Z*/*E*	*Z*	*E*
a	Et	H	H	*a*	100	83	—	6.10[b]	5.13[b]
b	Et	Me	H	88	100	89	4:1	7.46	6.54
c	Me	Me	Me	89	100	90	—	—	—
d	Me	Et	H	89	100	74	3:1	7.30[c]	6.46
e	Me	Pr^n	H	95	92	93	2:1	7.40	6.42
f	Me	Pr^i	H	95	99	79	1:1	7.03[c]	6.29
g	Me	$-(CH_2)_4-$		93	100	69	—	—	—

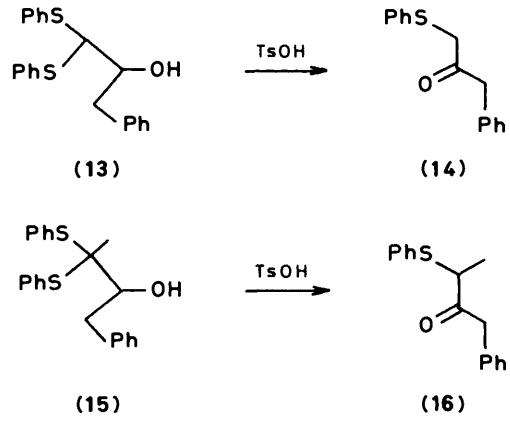
[a] Ref. 26. [b] Ref. 20. [c] Ref. 3.

(**1c**) by an unrelated route[23] and obtained the *Z*-isomer alone: the present route gives a 2:1 *Z*:*E* mixture. The unsubstituted ketone (**1a**), which is Takaki's arannulating agent,[8] can also be made by this route as 3-bromobutan-2-one is available, but (**1a**) dimerises by a Diels-Alder reaction, as others have found,[16] and Takaki's method[17] is the only reliable one.



In other cases where the carbon skeleton is unsymmetrical, our regiospecific route[24] to α-phenylthio ketones can be used: ketones (**14**) and (**16**) were made by this method, and ketone (**18**) has already been reported.[24] The ketone (**18**) was oxidised to its sulphoxide (**19**) and the Pummerer elimination route used to make the α-phenylthio enone (**1b**) in 89% yield as a 30:1 mixture of *Z*:*E*-isomers.

Unsymmetrical ketones may also be made by alkylation; thus the ketone (**18**) can be made by ethylation of phenylthio acetone, the PhS group directing enolate ion formation. The benzyl ketones (**14**) and (**16**) are particularly interesting cases as phenyl and PhS groups offer comparable anion stabilisation, α-PhS compounds (esters, amides and nitriles)[25] having pK_a



values *ca.* one pH unit lower than those of the corresponding α-phenyl compounds. Attempted methylation of the anion of the ketone (**14**) gave a mixture of methylated products which were not separated. The monomethyl compound (**16**) was available by our route from (**15**) and methylation occurred exclusively on the phenyl side to give (**20**) in 81% yield. A second methylation, however, occurred entirely on the PhS side to give (**21**) in 78% yield, showing that the small destabilisation given to the enolate by a methyl group is enough to tip the balance one way or the other.

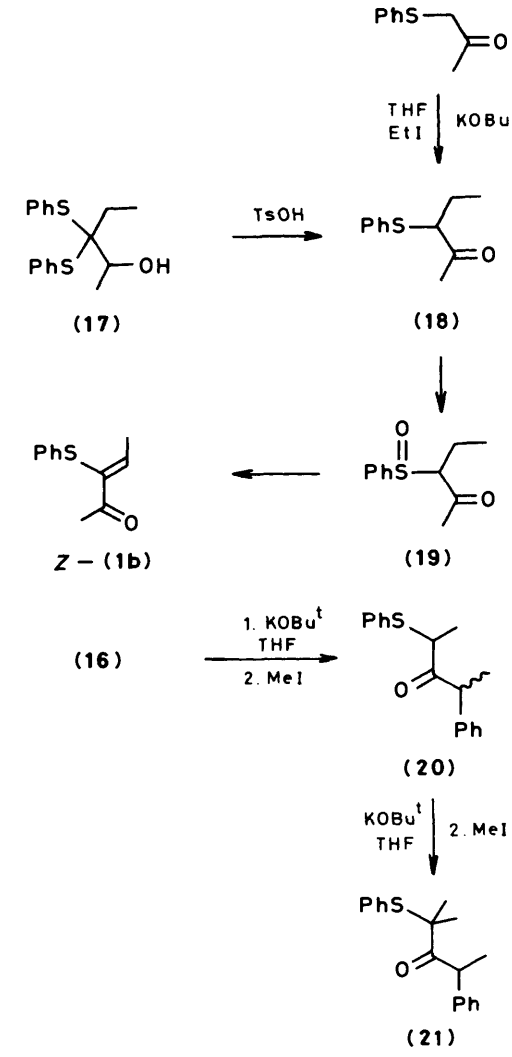
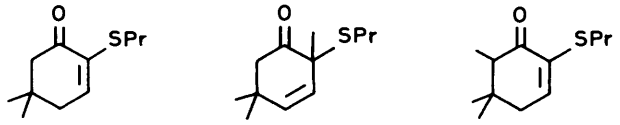


Table 2. Synthesis of α-phenylthio enones (1)

R¹	R²	R³	Intermediates yield	Product	Z/E	Yield (%)	δ_H(vinyl) Z	δ_H(vinyl) E
Me	H	H	(12) 99%	(1a)	—	*a*	6.07[b]	5.27[b]
Me	Me	H	(18) 80%[c] 65%[d]; (19) 73%	(1b)	30:1	89	7.31	6.52
Ph	Et	H	(9) 100%; (10) 93%; (11) 100%	(1c)	2:1	69	6.70	6.31

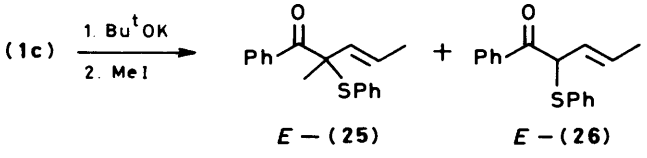
[a] Dimer isolated. [b] See ref. 17. [c] From (17) by rearrangement, see ref. 24. [d] By alkylation of phenylthioacetone.

Alkylation of the extended enolate from the cyclic α-propylthio enone (**22**) has been reported[14] to give predominantly the α-product (**23**) in contrast to the formation of the α′-product (**24**) from the kinetic enolate. The best conditions for extended enolate formation were Bu^{t}OK in Bu^{t}OH, followed by HMPA and then MeI. Other conditions gave mixtures of α- and α′-methylated products. We attempted a similar methylation of the simpler α-phenylthiocyclohexenone (**7**) using *N,N,N,N*-tetramethylethylenediamine (TMEDA) as co-solvent but obtained a mixture of products.



(22) (23) (24)

Alkylation of the open chain α-phenylthio enone (**1c**) was more successful, probably because the α′-position is blocked. The extended enolate was formed with Bu^{t}OK in tetrahydrofuran (THF) and quenched with MeI to give 41% methylated ketone *E*-(**25**) and 12% deconjugated ketone *E*-(**26**), presumably from protonation of the extended enolate. When TMEDA was added to the base before the enone, only polymerisation occurred, but when TMEDA was added after anion formation and before addition of MeI, the yield of product *E*-(**25**) improved to 61%. It appears that PhS groups are only marginally anion-stabilising enough to control reactions of extended enolated from enones. In the next paper[10] we describe related results with the esters (**2**).



E − (25) *E* − (26)

Experimental

General experimental details have been reported.[26] T.l.c. solvent systems 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). ^{13}C N.m.r. signals marked with an asterisk belong to *ortho* or *meta* carbons and are of double intensity.

Methyl 2-Bromopentanoate (**4d**).—Pentanoic acid (50 g, 0.49 mol) was added to refluxing thionyl chloride (67.8 g, 40.4 ml, 0.57 mol) and the mixture refluxed for a further 30 min. Then bromine (96.4 g, 31 ml, 0.60 mol) and phosphorus tribromide (5 ml) were added and refluxing continued until the red colour disappeared. The mixture was added dropwise to dry methanol (45.8 g, 58 ml, 1.43 mmol) and the solution refluxed for 30 min. After cooling, a few crystals of sodium thiosulphate were added, the mixture filtered, and the filtrate evaported under reduced pressure. Distillation of the residue gave the α-bromo ester (49.3 g, 52%) as an oil, b.p. 88—100 °C/27 mmHg (lit.,[27] b.p. 66 °C/22 mmHg), R_F(CH_2Cl_2) 0.6.

Also prepared by this method were the following: methyl 2-bromo-4-methylpentanoate (**4f**), as an oil[28] (54%), b.p. 78—80 °C/17 mmHg, R_F(CH_2Cl_2) 0.63; and methyl 2-bromo-2-cyclopentyl acetate (**4g**), as an oil[29] (83%), b.p. 64—66 °C/0.3 mmHg, R_F(CH_2Cl_2) 0.67.

2-Bromo-1-phenylpentan-1-one (**9**).—Valerophenone (23.86 g, 150 mmol) was added to a stirred suspension of anhydrous aluminium trichloride (0.15 g, 1.13 mmol) in dry ether (10 ml) under nitrogen at 0 °C. Bromine (23.55 g, 7.55 ml, 150 mmol) was added slowly, and then the mixture immediately concentrated under reduced pressure, diluted with ether (150 ml), and a few crystals of sodium thiosulphate added. The mixture was washed with water (50 ml) and brine (2 × 50 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the α-bromo ketone[30] (35.5 g, 100%) as an oil, R_F(CH_2Cl_2) 0.69.

Methyl 2-Phenylthiopentanoate (**5d**).—The α-bromoester (**4d**) (49 g, 0.25 mol) in ethanol (50 ml) was added slowly to a stirred solution of thiophenol (27.5 g, 25.6 ml, 0.25 mol) and sodium hydroxide (10 g, 0.25 mol) in ethanol (150 ml) under nitrogen. After 18 h the solution was concentrated under reduced pressure, diluted with water (200 ml), and extracted with ether (3 × 100 ml). The combined extracts were washed with aqueous sodium hydroxide (2 × 50 ml), water (2 × 20 ml), and brine (2 × 20 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was distilled to give the ester[31] (50 g, 89%) as an oil, b.p. 86—90 °C/0.1 mmHg, R_F(CH_2Cl_2) 0.53, $\nu_{max.}$(liquid film) 1 740 (CO_2Me) and 1 490 cm^{-1} (Ph); δ_H($CDCl_3$) 7.2—7.6 (5 H, m, PhS), 3.67 (1 H, t, *J* 8 Hz, PhSC*H*), 3.61 (3 H, s, MeO), 1.7—2.0 (2 H, m, PhSCHCH_2), 1.42 (2 H, tq, *J* 7, 7 Hz, MeCH_2), and 0.87 (3 H, t, *J* 7 Hz, *Me*CH_2) (Found: M^+, 224.0872. $C_{12}H_{16}O_2S$ requires *M*, 224.0873), *m/z* 224 (55%, M^+), 182 (5, PhSCH_2CO_2Me), 165 (60, *M* − CO_2Me), 123 (100, PhSCH_2), 110 (30, PhSH), and 109 (25, PhS). Also prepared by this method were the following.

Methyl 4-methyl-2-phenylthiopentanoate (**5f**). The bromide (**4f**) gave the *ester* (95%) as an oil, b.p. 80—84 °C/0.5 mmHg, R_F(CH_2Cl_2) 0.62; $\nu_{max.}$(liquid film) 1 740 (CO_2Me), 1 585, and 1 575 cm^{-1} (Ph); δ_H($CDCl_3$) 7.2—7.5 (5 H, m, PhS), 3.69 (1 H, t, *J* 7 Hz, PhSC*H*), 3.57 (3 H, s, MeO), 1.5—1.9 (3 H, m, Me_2CHCH_2), and 0.87 and 0.85 (each 3 H, d, *J* 7 Hz, *Me*CH) (Found: M^+, 238.1031. $C_{13}H_{18}O_2S$ requires *M*, 238.1027), *m/z* 238 (20%, M^+), 123 (50, PhSCH_2), and 110 (100, PhSH).

Methyl 2-cyclopentyl-2-phenylthioacetate (**5g**). The bromide (**4g**) gave the *ester* (93%) as an oil, b.p. 98—117 °C/0.1 mmHg, R_F(CH_2Cl_2) 0.6; $\nu_{max.}$(liquid film) 1 740 (CO_2Me), 1 590, and 1 580 cm^{-1} (Ph); δ_H($CDCl_3$) 7.2—7.6 (5 H, m, PhS), 3.65 (3 H, s, MeO), 3.51 (1 H, d, *J* 10 Hz, PhSC*H*), and 1.2—2.5 (9 H, m, cyclopentyl ring protons) (Found: M^+, 250.1024. $C_{14}H_{18}O_2S$

requires *M*, 250.1028); *m/z* 250 (80%, M^+), 191 (52, *M* − CO_2Me), 182 (18, $PhSCH_2CO_2Me$), 141 (22, *M* − PhS), 123 (60, $PhSCH_2$), 110 (52, PhSH), 109 (20, PhS), and 81 (100, *M* − PhSH − CO_2Me).

Methyl 3-methyl-2-phenylthiobutanoate (**5c**). The bromide (**4c**) gave the *ester* as an oil (26.9 g, 89%), b.p. 70—72 °C/0.05 mmHg, R_F(B) 0.52; $\nu_{max.}$(liq) 1 735 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.1—7.5 (5 H, m, PhS), 3.57 (3 H, s, CO_2Me), 3.41 (1 H, d, *J* 9 Hz, CHC*H*CO), 2.3—1.9 (1 H, m, CHC*H*Me_2), and 1.08 and 1.18 (3 H, each d, *J* 6.5 Hz, CHMe_2) (Found: M^+, 224.882, $C_{12}H_{16}O_2S$ requires *M*, 224.0871); *m/z* 224 (70%), 165 (100, *M* − CO_2Me), and 110 (45, $PhSH^+$).

Methyl 2-phenylthiohexanoate (**5e**). The bromide (**4e**) gave the *ester* as an oil (115 g, 95%), R_F(B) 0.51, $\nu_{max.}$(liq) 1 742 cm^{-1} (C=O), $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m, PhS), 3.65 (3 H, s, CO_2Me), 3.65 (1 H, t, *J* 7 Hz, CHC*H*CO), 7.8—9.2 (9 H, m, rest) (Found: M^+, 238.1003, $C_{13}H_{18}O_2S$ requires *M*, 238.1010), *m/z* 238 (40%), 179 (55, *M* − CO_2Me), 123 (100, $PhSCH_2^+$), and 109 (35, PhS^+).

1-Phenyl-2-phenylthiopentan-1-one (**10**). The bromide (**9**) gave the ketone (93%) as needles, m.p. 35—37 °C [from light petroleum (b.p. 30—40 °C)], $R_F(CH_2Cl_2)$ 0.63, $\delta_H(CDCl_3)$ 7.9—8.1 and 7.2—7.6 (10 H, m, PhS and PhCO), 4.48 (1 H, t, *J* 7.5 Hz, PhSC*H*), 1.8—2.2 (2 H, m, PhSCHCH_2), 1.3—1.7 (2 H, m, MeCH_2), and 0.91 (3 H, t, *J* 7 Hz, *Me*CH_2) (Found: M^+, 270.1069. $C_{17}H_{18}OS$ requires *M*, 270.1059), *m/z* 270 (18%, M^+), 265 (85, *M* − PhCO), 123 (100, $PhSCH_2$), 109 (12, PhS), 105 (65, PhCO), and 77 (59, Ph).

Ethyl 2-Phenylthiobut-2-enoate (**2b**).—Sodium periodate (85 g, 398 mmol) in water (700 ml) was added to a stirred solution of the sulphide (**5b**) (17.84 g, 79.6 mmol) in methanol (600 ml) under nitrogen at 0 °C. The mixture was allowed to warm up to room temperature over 18 h, when it was filtered and the precipitate washed with methanol. The combined filtrate and washings were concentrated under reduced pressure, diluted with brine (100 ml), and extracted with ether (4 × 100 ml). The combined extracts were washed with brine (2 × 100 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give ethyl 2-phenylsulphinylbutanoate (**6b**) (17.58 g, 92%) as an oil, $R_F(CH_2Cl_2)$ 0.05, which was dissolved in a solution of acetic anhydride (11.9 g, 11 ml, 116 mmol) and methanesulphonic acid (0.9 g, 0.68 ml, 9 mmol) in dichloromethane (500 ml) and stirred at 40 °C for 8 h. The cooled solution was concentrated under reduced pressure, diluted with water (150 ml), and extracted with ether (4 × 40 ml). The combined extracts were washed with water (2 × 40 ml), aqueous sodium hydrogen carbonate (4 × 40 ml), and brine (2 × 30 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was distilled to give the unsaturated ester (**2b**) (10.9 g, 67%) as an oil, b.p. 90 °C/0.05 mmHg, $R_F(CH_2Cl_2)$ 0.53, see below. Also prepared by this method were the following.

Methyl 2-phenylthiopent-2-enoate (**2d**). Oxidation of the sulphide (**5d**) with sodium periodate gave methyl 2-phenylsulphinylpentanoate (**6d**) (100%) as an oil, $R_F(CH_2Cl_2)$ 0.04, 0.07 (2 diastereoisomers), which gave the unsaturated ester (74%) as a mixture of geometrical isomers, of which only the *Z*-isomer has been previously reported,[3] b.p. 98—102 °C/0.3 mmHg (lit.,[3] 60—70 °C/1 mmHg), $R_F(CH_2Cl_2)$ 0.54. *E-isomer*: $R_F(CH_2Cl_2)$ 0.61, $\nu_{max.}$(liquid film) 1 725 (CO_2Me), 1 610, and 1 590 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.218 (5 H, br s, PhS), 6.46 (1 H, t, *J* 7.5 Hz, C=CH), 3.63 (3 H, s, MeO), 2.50 (2 H, dq, *J* 7.5, 7.5 Hz, MeCH_2), and 1.03 (3 H, t, *J* 7.5 Hz, *Me*CH_2) (Found: M^+, 222.0696. $C_{12}H_{14}O_2S$ requires *M*, 222.0714); *m/z* 222 (90%, M^+), 190 (100, *M* − MeOH), and 163 (12, *M* − CO_2Me).

Methyl 4-methyl-2-phenylthiopent-2-enoate (**2f**). Oxidation of sulphide (**5f**) with sodium periodate gave methyl 4-methyl-2-phenylsulphinylpentanoate (**6f**) (99%) as an oil, $R_F(CH_2Cl_2)$ 0.03, 0.05 (2 diastereomers), which gave a mixture of geometrical isomers of the unsaturated ester (79%) of which only the *Z*-isomer has been previously reported,[3] $R_F(CH_2Cl_2)$ 0.52. E-*isomer* $R_F(CH_2Cl_2)$ 0.61, $\nu_{max.}$(liquid film) 1 720 (CO_2Me), 1 610 (C=C), 1 585, and 1 480 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.2—7.3 (5 H, br s, PhS), 6.29 (1 H, d, *J* 11 Hz, C=CH), 3.63 (3 H, s, MeO), 3.17 (1 H, d septet, *J* 11, 7 Hz, Me_2CH), and 1.03 (6 H, d, *J* 7 Hz, Me_2CH) (Found: M^+, 236.0868. $C_{13}H_{16}O_2S$ requires *M*, 236.0871), *m/z* 236 (43%, M^+), 204 (45, *M*— MeOH), and 99 (100, *M*—PhS—CO).

Methyl cyclopentylidenephenylthioacetate (**2g**). Oxidation of sulphide (**5g**) gave methyl 2-cyclopentyl-2-phenylsulphinylacetate (6 g) (100%) as an oil, which gave the ester[3] (69%) as an oil, b.p. 126—136 °C/0.1 mmHg (lit.,[3] 130—150 °C/1 mmHg), R_F (CH_2Cl_2) 0.57, and 1-phenyl-2-phenylthiopent-2-en-1-one (**1c**). Oxidation of sulphide (**10**) gave 1-phenyl-2-phenylsulphinylpentan-1-one (**11**) (100%) as an oil, $R_F(CH_2Cl_2)$ 0.03—0.05 which gave a mixture of geometrical isomers (*E*:*Z* 1:2) of the ketone (69%), as an oil, b.p. 134—137 °C/0.5 mmHg, of which only the *Z*-isomer, $R_F(CH_2Cl_2)$ 0.52 had been reported previously.[24] E-*isomer*, $R_F(CH_2Cl_2)$ 0.62, $\nu_{max.}$(liquid film) 1 685 (C=O), 1 600, and 1 580 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.8—8.0 and 7.1—7.6 (10 H, m, PhS and PhCO), 6.31 (1 H, t, *J* 8 Hz, C=CH), 2.13 (2 H, dq, *J* 8, 7 Hz, MeCH_2), and 0.99 (3 H, t, *J* 7 Hz, *Me*CH_2); $\delta_C(CDCl_3)$ 194.0 (s, C=O), 143.9, 133.2, 130.9*, 129.4*, 128.9*, 128.4*, and 127.2 (aromatic and olefinic), 24.1 (t, CH_2), and 13.7 (q, Me) (Found: M^+, 268.0923. $C_{17}H_{16}OS$ requires *M*, 268.0922); *m/z* 268 (66%, M^+), 163 (12, *M* − PhCO), 159 (21, *M* − PhS), 109 (17, PhS), 105 (100, PhCO), and 77 (88, Ph).

3-Phenylsulphinylbutan-2-one (**12**).—Oxidation of 3-phenylthiobutan-2-one gave the sulphoxide (**12**) (99%) as an oil, R_F [3:7, acetone–light petroleum (b.p. 40—60 °C)] 0.17; $\nu_{max.}$(film) 1 710 (C=O), 1 580 and 1 480 (PhS), and 1 050 cm^{-1} (S=O); $\delta_H(CDCl_3)$ 7.6 (5 H, m, Ph), 3.9 (1 H, q, MeC*H*S), 2.3 (3 H, s, MeCO), and 1.4 (3 H, 2 d, *J* 6 Hz, *Me*CH); *m/z* 196 (M^+, 37%), 180 (2), 126 (88), 125 (100), 110 (50), and 78 (93). Treatment with Ac_2O *etc.*, gave the Diels-Alder dimer.[17]

Sulphoxide Synthesis with MCPBA.—A solution of *m*-chloroperbenzoic acid (80% grade; 38 g, 0.17 mol) in dry ether (170 ml) was added slowly to a stirred, cooled (0 °C) solution of the sulphide (0.17 mol) in dry ether (500 ml) under a nitrogen atmosphere. The resultant suspension was stirred for a further 0.5 h at 0 °C, condensed, diluted with dichloromethane, and then washed with aqueous sodium thiosulphate (3 × 150 ml), aqueous sodium hydrogen carbonate (3 × 150 ml), and brine (2 × 100 ml), and dried ($MgSO_4$). Solvent removal under reduced pressure gave the sulphoxide as a mixture of diastereoisomers which were used without purification. In this way, the following were prepared.

3-Phenylsulphinylpentan-2-one (**19**). The *ketone* was an oil (73%), purified by column chromatography eluting with light petroleum (b.p. 40—60 °C)–ether, as a mixture of diastereoisomers, R_F(ether) 0.35; $\nu_{max.}$(liq) 1 715 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.7—7.4 (5 H, m, PhS), 3.69 (1 H, dd, *J* 8, 6.5 Hz, C*H*COMe, one isomer), 3.51 (1 H, dd, *J* 8, 7.5 Hz, C*H*COMe, one isomer), 2.13 and 1.95 (3 H, s, MeCO, each isomer), 7.8—8.3 (2 H, m, MeCH_2*CH, both isomers), and 9.1 (3 H, br t, *J* 7 Hz, *Me*CH_2, both isomers) (Found: M^+, 210.0716. $C_{11}H_{14}O_2S$ requires *M*, 210.0715); *m/z* 210 (5%), 125 (40, $PhSOH^+$), 125 (30, $PhSO^+$), and 110 (40, $PhSH^+$).

Ethyl 2-phenylsulphinylpropanoate (**6a**). The ester was an oil[20] (100%), not purified further, a mixture of diastereoisomers M and N, R_F(C) 0.21, 0.18; $\nu_{max.}$(liq.) 1 738 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.5 (5 H, br s, PhS), 4.05 (2 H, q, *J* 7 Hz, CO_2CH_2Me), 3.75 (N) and 3.49 (M) (1 H, q, *J* 7 Hz, C*H*Me), 1.46 (M) 1.32 (N) (3 H, d, *J*

7 Hz, CH*Me*), and 1.20 (3 H, t, *J* 7 Hz, OCH_2Me); *m/z* 226 (50%, M^+), 126 (75, $PhSOH^+$), and 125 (199, $PhSO^+$).

Ethyl 2-phenylsulphinylbutanoate (**6b**). The ester was an oil (10%), not purified further, a mixture of diastereoisomers, R_F(C) 0.20, 0.15; $\nu_{max.}$(liq) 1 735 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.7—7.4 (5 H, m, PhS), 4.3—3.8 (2 H, m, CO_2CH_2*Me), 3.58—3.34 [1 H, m, PhS(O)C*H*], 2.3—1.7 (2 H, m, $CHCH_2$*Me), and 1.3—0.9 (6 H, m, both MeSO) (Found: M^+, 240.0818 $C_{12}H_{16}O_3S$ requires *M*, 240.0820), *m/z* 240 (20%), 222 (20, *M* − H_2O), 126 (100, $PhSOH^+$), 125 (55, $PhSO^+$), 115 (80 *M* − PhSO), 110 (60, $PhSH^+$), and 109 (40, PhS^+).

Methyl 3-methyl-2-phenylsulphinylbutanoate (**6c**). The *ester* was an oil (100%), not purified further, a mixture of diastereoisomers M and N, R_F(C) 0.55, 0.45; $\nu_{max.}$(liq) 1 735 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.7—7.3 (5 H, m, PhS), 3.43 (M) and 3.41 (N) (3 H, s, CO_2Me), 3.44 (M) (1 H, d, *J* 8 Hz, $CHCO_2$), 3.16 (N) (1 H, d, *J* 9.5 Hz, $CHCO_2$), 2.9—2.3 (1 H, m, C*H*Me_2), and 1.23, 1.20 (M) and 1.32, 1.08 (N) (each 2 × 3 H, d, *J* 7 Hz, Me_2CH) (Found: M^+, 240.0813. $C_{12}H_{16}O_3$ requires *M*, 240.0820); *m/z* 240 (10%), 126 (90, $PhSOH^+$), 125 (48, $PhSO^+$), 115 (80, *M* − PhSO), and 110 (100, $PhSH^+$). This compound was also prepared by oxidation of the α-phenylthio ester using sodium periodate in methanol–water. The product was an oil (83%) separated into the individual isomers M and N by p.l.c.

Methyl 2-phenylsulphinylhexanoate (**6e**). The *ester* was an oil (92%), purified by column chromatography eluting with light petroleum (b.p. 40—60 °C)–ether, a small sample of which was separated into the individual diastereoisomers M and N by p.l.c. The mixture was an oil, R_F(C) 0.23 (M), 0.16 (N), $\nu_{max.}$(liq.) 1 740 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.6—7.3 (5 H, m, PhS), 3.56 (N) and 3.48 (M) (3 H, s, CO_2Me), 3.56 (N) and 3.45 (M) [1 H, t, *J* 8.5 (M), 7 (N) Hz, $CHCO_2$], 2.4—1.2 (M) and 2.2—1.0 (N) (6 H, m, CH_2's), and 1.1—0.8 (M) and 1.1—0.7 (N) (3 H, m, $MeCH_2$) (Found: M^+, 254.0977. $C_{13}H_{18}O_3S$ requires *M*, 254.0973) *m/z* 254 (2%), 129 (85, *M* − PhSO), 126 (70, $PhSOH^+$) 125 (100, $PhSO^+$), 110 (15, $PhSH^+$), and 109 (PhS^+).

Pummerer Eliminations on the Sulphoxides.—The sulphoxide (63 mmol) in dichloromethane (700 ml) containing acetic anhydride (10 g, *ca.* 0.1 mol) and methanesulphonic acid (1 g, *ca.* 10 mmol) was heated at 40 °C for 2 h under a nitrogen atmosphere. The cooled solution was evaporated under reduced pressure, the temperature not being allowed to exceed 35 °C, then diluted with water (200 ml), and extracted with ether (2 × 50 ml). The organic extracts were washed with water (2 × 50 ml), aqueous sodium hydrogen carbonate (3 × 40 ml), and brine (2 × 40 ml), and dried ($MgSO_4$). Solvent removal under reduced pressure followed by chromatography of the resultant oil, eluting with light petroleum (b.p. 30—40 °C)–ether, gave the product. In this way the following were prepared.

3-Phenylthiopent-3-en-2-one (**1b**). The ketone, a mixture of isomers (*Z*:*E* = 30:1), was an oil (89%), R_F(C) 0.5 (minor), 0.45 (major); $\nu_{max.}$(liq.) 1 685 (C=O) and 1 601 cm^{-1} (C=C), the *Z* isomer has been reported,[32] the *E* isomer had $\delta_H(CDCl_3)$ (5 H, m, PhS), 6.52 (1 H, q, *J* 7.5 Hz, MeC*H*=C), 2.25 (3 H, s, COMe), and 7.96 (3 H, d, *J* 7.5 Hz, *Me*CH=C) (Found: M^+, 192.0631. $C_{11}H_{12}OS$ requires *M*, 192.0906); *m/z* 192 (100%), 149 (95), 134 (60), 110 (40, $PhSH^+$), and 109 (40, PhS^+).

Ethyl 2-phenylthiobut-2-enoate (**2b**). The ester† (89%) was an oil, b.p. 96—98 °C/0.4 mmHg, and was a mixture of isomers (*Z*:*E* = 4:1), R_F(B) 0.52 (minor) and 0.48 (major); $\nu_{max.}$(liq.) 1 725, 1 715 (C=O), and 1 618 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 7.1—7.3 (5 H, m, PhS), 7.46 (*Z*) and 6.54 (*E*) (1 H, q, *J* 7.5 Hz, MeC*H*=C), 5.90 (2 H, q, *J* 7 Hz, CO_2CH_2Me), 7.92 (3 H, d, *J* 7.5 Hz, *Me*CH=C), and 8.92 (3 H, t, *J* 7 Hz, CO_2CH_2Me) (Found: M^+, 222.0748. $C_{12}H_{14}O_2S$ requires *M*, 222.0715) *m/z* 222 (50%), 192 (40, *M* − H, Et), 149 (70, *M* − CO_2Et), 134 (45, *M* − Me, CO_2Et), 115 (50, *M* − PhS), and 110 (50, $PhSH^+$).

Methyl 3-methyl-2-phenylthiobut-2-enoate (**2c**). The ester (90%) was an oil, b.p. 78—82 °C/0.3 mmHg (lit.,[3] b.p. 130 °C/3 mmHg), R_F(B) 0.45.

Methyl 2-phenylthiohex-2-enoate (**2e**). The *ester* (93%) was an oil, b.p. 84—86 °C/0.4 mmHg, and was a mixture of isomers (*Z*:*E* = 2:1), R_F(B) 0.54 (minor), 0.44 (major), $\nu_{max.}$(liq.) 1 720 (C=O) and 1 615 (C=C); $\delta_H(CDCl_3)$ 7.0—7.3 (5 H, m, PhS), 7.40 (*Z*) and 6.42 (*E*) (1 H, t, *J* 7.5 Hz, CH_2CH=C), 3.60 (3 H, s, CO_2Me), 2.50 (2 H, br d t, *J* 7, 7.5 Hz, CH_2CH=C), 8.2—8.8 (2 H, m, $MeCH_2$), and 9.04 (3 H, br t, *J* 7 Hz, $MeCH_2$) (Found: M^+, 236.0871. $C_{13}H_{16}O_2S$ requires *M*, 236.0896); *m/z* 236 (70%), 204 (50, *M* − MeOH), 175 (30, *M* − H, CO_2Me, H), 147 (100, *M* − H, CO_2Me, Et), 110 (60, $PhSH^+$), and 109 (40, PhS^+).

3-Phenylthiopentan-2-one (**18**) *by Alkylation.*—Phenylthioacetone (5 g, 0.03 mol) in dry THF (30 ml) was added to a stirred, cooled (0 °C) solution of potassium t-butoxide (3.4 g, 0.033 mol) in dry THF (30 ml) under a nitrogen atmosphere. After 0.5 h, ethyl iodide (5 g, slight excess) in THF (5 ml) was added and the solution stirred and allowed to reach room temperature (2 h); it was then heated under reflux (2 h). The cooled solution was condensed under reduced pressure, diluted with water (100 ml), and extracted with dichloromethane (3 × 50 ml). The organic extracts were washed with brine (2 × 30 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure. The resultant oil was purified by chromatography, eluting with light petroleum (b.p. 40—60 °C)–ether followed by distillation to give the ketone (65%) as a pale yellow oil b.p. 76—82 °C/0.4 mmHg, R_F(B) 0.35; spectroscopic data were identical to those of a sample prepared[24] by rearrangement of (**17**).

1-Phenyl-3,3-bis(phenylthio)butan-2-ol (**15**).—Butyl-lithium (1.5M solution in hexane; 1.3 ml, 2 mmol) was slowly added to a stirred, cooled (−10 °C) solution of bisphenylthioethane (0.42 g, 2 mmol) in dry THF (10 ml) under a nitrogen atmosphere. After 15 min the anion was quenched with phenylacetaldehyde in dry THF (50% w/v) until the yellow colour was just discharged. The procedure was repeated twice, 0.5 h being allowed between each addition, using butyl-lithium (0.2 ml). The solution was then left for 2 h at room temperature after which it was diluted with water (50 ml) and extracted with dichloromethane (3 × 20 ml). The combined organic extracts were washed with water (2 × 15 ml) and brine (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The product was purified by p.l.c. [eluting with ether–light petroleum (b.p. 40—60 °C)] to give the *adduct* (0.55 g, 75%) as needles, m.p. 89—90 °C [from ether–light petroleum (b.p. 30—40 °C)], R_F(B) 0.25; $\nu_{max.}$(Nujol) 3 600—3 200 cm^{-1} (OH); $\delta_H(CDCl_3)$ 7.1—7.7 (15 H, m, Ph and PhS), 3.83 (1 H, dd, *J* 10, 2.5 Hz, C*H*OH), 3.30 and 2.94 (2 H, ABX system, J_{AB} 14, J_{AX} 2.5, J_{BX} 10 Hz, $PhCH_2CH$), and 2.94 and 1.34 (3 H, s, Me); *m/z* 366 (0.1%, *M*), 257 (100, *M* − PhS), and 110 (55, $PhSH^+$) (Found: C, 71.9; H, 6.00; S, 17.8. $C_{22}H_{22}OS_2$ requires C, 72.1; H, 6.05; S, 17.5%). Also prepared in this way was the following.

1-Phenyl-3,3-bis(phenylthio)propan-2-ol (**13**). The *alcohol* was an oil (4.9 g, 70%), R_F(B) 0.25; $\nu_{max.}$(liq.) 3 600—3 200; $\delta_H(CDCl_3)$ 7.1—7.5 (15 H, m, Ph and PhS), 4.44 [1 H, d, *J* 3.5 Hz, $(PhS)_2CH$CH], 4.07 (1 H, ddd, *J* 7.5, 6.0, 3.5 Hz, CHC*H*OH), and 3.21 and 2.97 (2 H, ABX system, J_{AB} 14, J_{AX} 6, J_{BX} 7.5 Hz, $PhCH_2CH$) (Found: M^+, 352.0956. $C_{21}H_{20}S_2$ requires *M*, 352.095); *m/z* 352 (18%), 243 (30, *M* − PhS), and 110 (100, $PhSH^+$).

† The ester reported by Uda[2] must be the *Z*-isomer; the *E*-isomer has not been reported.

1-*Phenyl*-3-*phenylthiobutan*-2-*one* (**16**).—1-Phenyl-3,3-bis-(phenylthio)butan-2-ol (2.3 g, 8 mmol) in benzene (50 ml) containing toluene-*p*-sulphonic acid monohydrate (1.2 g, 8 mmol) was heated under reflux in a nitrogen atmosphere for 10 min. The mixture was poured onto crushed ice—10% aqueous sodium hydroxide (total 250 ml), extracted with dichloromethane (3 × 70 ml), and the combined organic layers washed with brine (2 × 50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The product was purified by column chromatography [eluting with ether–light petroleum (b.p. 40—60 °C)] to give the *ketone* (1.15 g, 72%) as a yellow oil, R_F(B) 0.45; $\nu_{max.}$(liq.) 1 710 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.1—7.5 (10 H, m, Ph and PhS), 3.88 (2 H, s, PhCH_2), 3.81 (1 H, q, *J* 7 Hz, PhSC*H*Me), and 1.35 (3 H, d, *J* 7 Hz, CH*Me*); *m/z* 256 (18%, *M*), 218 (20, $PhSSPh^+$), 137 (100, $PhSCHMe^+$), 109 (50, PhS^+), and 91 (55, $PhCH_2^+$) (Found: C, 75.0; H, 6.35; S, 12.7. $C_{16}H_{16}OS$ requires C, 75.0; H, 6.30; S, 12.5). Also prepared in this way was the following.

1-*Phenyl*-3-*phenylthiopropan*-2-*one* (**14**). The *ketone* was an oil (95 mg, 79%), R_F(B) 0.40, $\nu_{max.}$(liq.) 1 715 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.04—7.39 (10 H, m, Ph and PhS), 3.85 (1 H, s, PhCH_2), and 3.66 (2 H, s, PhSCH_2) (Found: M^+, 2 452.0765. $C_{15}H_{14}OS$ requires *M*, 242.0767); *m/z* 242 (57%), 133 (55, *M* − PhS), 123 (100, $PhSCH_2^+$), and 91 (95, $PhCH_2^+$).

Alkylation of 1-*Phenyl*-3-*phenylthiopropan*-2-*one* (**14**).—1-Phenyl-3-phenylthiopropan-2-one (0.242 g, 1 mmol) in dry THF (5 ml) was added dropwise to a stirred, cooled (0 °C) solution of potassium t-butoxide (0.12 g, 1 mmol) in dry THF (5 ml) under nitrogen. After 0.5 h, an excess of methyl iodide was added and the mixture left at room temperature (18 h). The solution was poured into water (30 ml), extracted with dichloromethane (4 × 10 ml), and the extract washed (brine 2 × 10 ml) and dried ($MgSO_4$). Solvent removal gave an oil (0.26 g) which was shown by n.m.r. and t.l.c. to be a mixture of composition; starting ketone (20%), the two monomethylated products (30% each), and the two isomers of the dimethylated product (20% total). No separation was attempted.

2-*Phenyl*-4-*phenylthiopentan*-3-*one* (**20**).—1-Phenyl-3-phenylthiobutan-2-one (0.155 g, 0.6 mmol) in dry THF (5 ml) was added to a stirred, cooled (0 °C) solution of potassium t-butoxide (0.07 g, 0.6 mmol) in dry THF (5 ml) under nitrogen. After 0.5 h, an excess of methyl iodide was added and the solution left overnight. The mixture was diluted with water (30 ml) and extracted with dichloromethane (4 × 10 ml). The washed (brine 2 × 10 ml) and dried ($MgSO_4$) extracts were evaporated and the residue purified by p.l.c. to give the *ketone* as a mixture of isomers M and N (0.134 g, 81%); R_F 0.58 (major) and 0.55 (minor); $\nu_{max.}$(liq) 1 715 cm^{-1} (C=O); $\delta_H(CDCl_3)$ (*ca.* 4:1), 7.0—7.5 (10 H, m, ArH), 4.56 (N) and 4.17 (M) (1 H, each q, *J* 7 Hz, PhC*H*CO), 3.85 (N) and 3.67 (M) (1 H, each q, *J* 7 Hz, PhSC*H*CO), and 1.18—1.50 (6 H, 4 d, *J* 7 Hz, MeS).

2-*Methyl*-4-*phenyl*-2-*phenylthiopentan*-3-*one* (**21**).—2-Phenyl-4-phenylthiopentan-3-one (0.54 g, 2 mmol) in dry THF (5 ml) was added dropwise to a stirred, cooled (0 °C) solution of potassium t-butoxide (0.225 g, 2 mmol) in dry THF (5 ml) under a nitrogen atmosphere. After 0.5 h an excess of methyl iodide was added and the mixture left at room temperature (18 h). The solution was diluted with water (30 ml) and extracted with dichloromethane (4 × 10 ml). The washed (brine 2 × 10 ml) and dried ($MgSO_4$) extracts were evaporated and the residue purified by p.l.c. to give the *ketone* as an oil (0.49 g, 78%) (Found: M^+, 284.1234. $C_{18}H_{20}OS$ requires *M*, 284.1247); *m/z* 284 (20%), 152 (80%, $PhSCHMe_2$), 151 (100%, $PhSCMe_2$), 110 (40%, PhSH), and 105 (70%, $PhCHCH_3$); R_F 0.62; $\nu_{max.}$(liq) 1 700 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 7.1—7.5 (10 H, m, ArH), 4.61 (1 H, q, *J* 7 Hz, PhC*H*Me), 1.51 (3 H, d, *J* 7 Hz, PhCH*Me*), and 1.29 and 1.38 (6 H, two s, PhSCMe_2).

(E)-2-*Methyl*-1-*phenyl*-2-*phenylthiopent*-3-*en*-1-*one* (**25**).—The enone (**16**) (407 mg, 1.52 mmol) in dry THF (1 ml) was added dropwise to a stirred solution of potassium t-butoxide (204 mg, 1.88 mmol) in dry THF (25 ml) under nitrogen at −20 °C. After 30 min TMEDA (213 mg, 1.83 mmol) was added, followed by methyl iodide (260 mg, 1.83 mmol) and the cooling bath was 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 *ketone* (**25**) (61%) as an oil, $R_F(CH_2Cl_2)$ 0.65; $\nu_{max.}$(liquid film) 1 680 (C=O), 1 605, 1 585 (Ph), and 970 cm^{-1} (trans HC=CH); $\delta_H(CDCl_3)$ 8.1—8.3 and 7.2—7.6 (10 H, m, PhS and PhCO), 5.99 (1 H, d, *J* 16 Hz, MeCH=C*H*), 5.71 (1 H, dq, *J* 16, 6.5 Hz, MeC*H*=CH), 1.71 (3 H, d, *J* 6.5 Hz, *Me*CH=CH) and 1.54 (3 H, s, PhSC*Me*); $\delta_C(CDCl_3)$ 197.9 (s, C=O), 136.9*, 132.3, 131.9, 131.0, 130.3*, 129.4, 129.3, 128.6*, 127.9*, 127.8 (aromatic and olefinic carbons), 60.8 (s, quaternary carbon), 25.2 (q, *Me*CSPh), and 18.2 (q, *Me*C=C) (Found: M^+, 282.1078. $C_{18}H_{18}OS$ requires *M*, 282.1078); *m/z* 282 (2%, M^+,), 177 (100, *M* − PhCO), 173 (10, *M* − PhS), 149 [10, PhSC(Me)CH], 144 (11, *M* − PhSH − C_2H_4), 110 (12, PhSH), 109 (11, PhS), 105 (40, PhCO), 77 (45, Ph), and 67 (11, *M* − PhSH − PhCO); and also (E)-1-*phenyl*-2-*phenylthiopent*-3-*en*-1-*one* (**26**) (12 mg, 8%) derived by α-protonation of the extended enolate anion, $R_F(CH_2Cl_2)$ 0.55, $\nu_{max.}$(liquid film) 1 680 (C=O), 1 600, 1 585 (Ph), and 965 cm^{-1} (*trans*-HC=CH); $\delta_H(CDCl_3)$ 7.9—8.1 and 7.3—7.6 (10 H, m, PhS and PhCO), 5.86 (1 H, dd, *J* 18, 8 Hz, MeCH=C*H*), 5.57 (1 H, dq, *J* 18, 5 Hz, MeC*H*=CH), 5.14 (1 H, d, *J* 8 Hz, PhSC*H*), and 1.67 (3 H, d, *J* 5 Hz, *Me*CH=CH) (Found: M^+, 268.0920. $C_{17}H_{16}OS$ requires *M*, 268.0922); *m/z* 268 (9%, M^+), 163 (10, *M* − PhCO), 159 (5, *M* − PhS), 135 (10, PhSCHCH), 130 (9, *M* − PhSH − C_2H_4), 110 (13, PhSH), 109 (11, PhS), 105 (68, PhCO), and 77 (37, Ph). Without TMEDA the methylated enone (**25**) was isolated in 41% yield, with 12% of the protonated enone (**26**).

Acknowledgements

We thank S.E.R.C. for grants (to J. D., J. I. G., and P. G. H.).

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Received 30*th December*, 1985; *Paper* 5/2269