# Lithium Keten Thioacetalides. Factors influencing α- *versus* γ-Alkylation [1]

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Alkylation of the lithium salt of the vinyl-1,3-dithian (2; R = CH_3) occurred exclusively at the α-carbon. However both α- and γ-alkylation was observed with the substrate (2; R = C_6H_5). A systematic investigation revealed that the α : γ ratio is correlated with the hardness of both the leaving group and the alkyl group of the alkylating agent. An occasionally formed side-product from the reactions of (2; R = C_6H_5) was the α,γ-dimer (11) of the anion (6; R = C_6H_5).

IN conjunction with an ongoing project, we required a general route to the substituted enones (1). The dithian method [2] (Scheme 1) was employed since vinyldithians are readily available from the corresponding aldehydes,[3] and alkylation followed by hydrolysis [4] should result in the desired products (1). Regioselectivity of electrophilic attack at the α position of dithian anions is well established.[2,4,5]


(2)

a; R = CH_3

b; R = C_6H_5

(3)

(1)
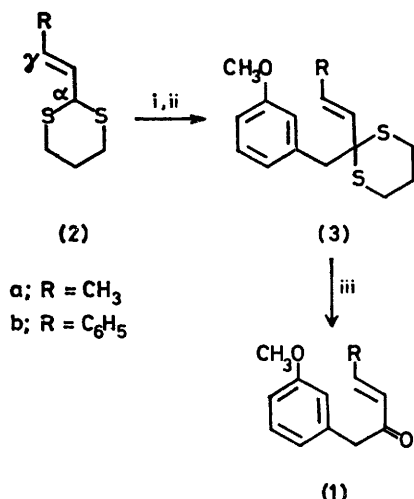
SCHEME 1 Reagents: i, base; ii, m-$CH_3OC_6H_4CH_2Br$; iii, hydrolysis

Using Seebach's method,[6] vinyldithians (2a and b) were prepared in 45 and 70% yield, respectively, from the corresponding aldehydes. However, milder reaction conditions, which involved a modification of Poulter's method,[7] gave (2b) in 95% yield. Alkylation of the anion of dithian (2a), gave the expected α-alkylation product (3a) in 50% yield. Fetizon's procedure [8] was used to hydrolyse (3a) to the enone (1a).

However, alkylation of the anion of dithian (2b) with m-methoxybenzyl bromide under the same conditions gave mainly the γ-alkylation product (4). N.m.r. analysis indicated a 9 : 1 ratio of (4) to (3b). The formation of the γ-alkylation product (4) was further confirmed by hydrolysis of its mercuric salt [4] to the acid (5). This result led us to investigate the reaction.

Keten thioacetalides (6) (Scheme 2) can serve two functions: (a) that of masked αβ-unsaturated acyl anion equivalents [4,5] *via* α-alkylation and (b) that of masked β-propionate anion equivalents *via* γ-alkylation (Scheme

2). The former application has been amply demonstrated,[4,5] whereas development of the latter role wherein rare umpolung [4] reactivity is conferred on the β-carbon of acyl groups has only recently begun.[9] Ziegler [9]
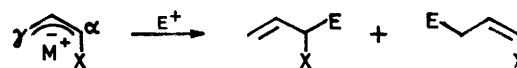

(4)

(5)
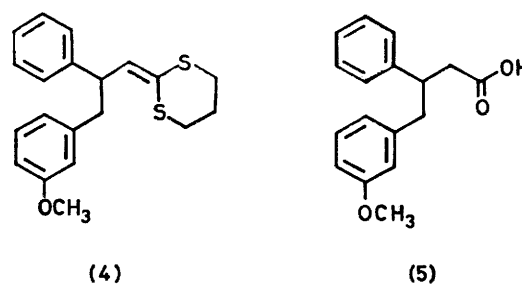
noted that γ-alkylation could be induced by employing Cu^I as metal cation. Furthermore, the synthetic value of 4-aryl-carboxylic acids, such as the hydrolysed products (5) is well documented.[10]

Keten thioacetalides (6) are prepared by suitable base treatment of either vinyldithians [7] (2) or keten thio-
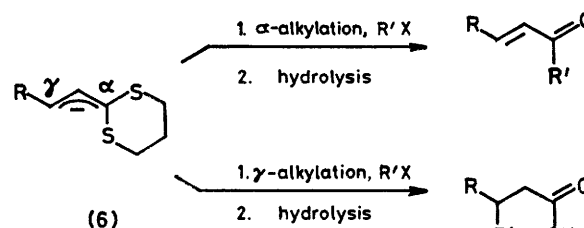
SCHEME 2

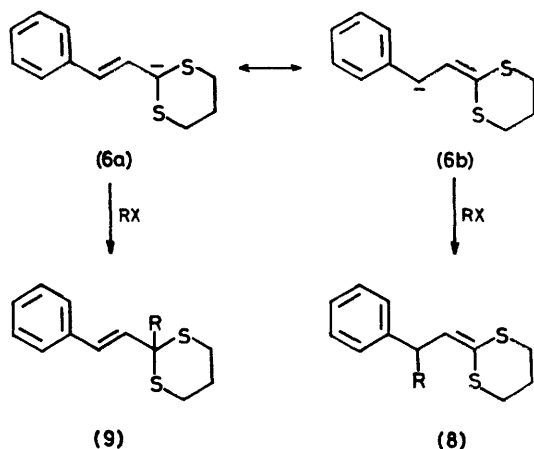
SCHEME 3

acetals (7).[4,5] The route chosen does not affect the orientation of alkylation. Electrophilic attack on the hetero-substituted allylic anions (Scheme 3; X = OR,[11] $OSiR_3$,[12] OTHP,[13] SR,[14] S^-,[15] BR_2,[16] NR_2,[17] SOR; [18] M^+ = Li^+,[11-13] Zn^{2+},[11] BR_3 complex [19]) has been investigated. Regioselectivity appears to depend on a number of factors, *e.g.* the nature of the electrophile,[9,11,12] the steric bulk of the alkylating agent,[1,12] the steric bulk of the substituents on the anion,[9] and the nature [11] and solvation [14] of the counterion. The applicability of the hard and soft acids and bases (HSAB) principle [20,21] to

this type of system has not been noted and was therefore investigated.

The anion (6; R = C_6H_5) is ambident [(6a) ←→ (6b), Scheme 4],[22] and α-C is harder than γ-C.[20] The results

(6a) **(6b)**

(9) **(8)**

SCHEME 4

of our alkylation studies are summarised in Table 1. The following conclusions can be made (a) the α : γ ratio increases with increasing hardness of both the leaving group (I⁻ < Br⁻ < Cl⁻ < OTs⁻ < SO_4^{2-})[20] and the acid[11] (PhCH$_2^+$ < CH$_3^+$ < CH$_3$CH$_2$CH$_2^+$ < H⁺ ⩽ SiMe$_3^+$)[20] and (b) the leaving group effect is greatest when R = Me.

The α-alkylation product (9) invariably has a *trans*-configuration. This has been reported by others.[22] By analogy,[11,12] an internally co-ordinated anion (10) is possible. If planar, it could explain *trans*-alkene formation. However exclusive γ-metallation would be expected to lead consistently to a low α : γ alkylation ratio. This is not observed. Ziegler[9] noted that the regioselectivity of alkylation of keten thioacetalides was

TABLE 1

Alkylation of anion (6; R = C_6H_5)

Entry	RX	Yield (%)[a] (8) + (9)	Ratio[b] (8) : (9)		Yield (%)[a] (11)	(2b)
1	m-CH₃OC₆H₄CH₂Br	69	90	10		
2	C₆H₅CH₂I	60	90	10		
3	C₆H₅CH₂Br	75	86	14		
4	C₆H₅CH₂Cl	66	78	22	22	
5	C₆H₅CH₂OTs[e]	74	74	26	c	d
6	Prⁿl	79	37	63	c	
7	PrⁿBr	57	27	73	10	d
8	CH₃I	60	44	56		
9	CH₃OTs	80	18	82	c	
10	(CH₃)₂SO₄	55		100	c	
11	(CH₃)₃SiCl	72		100	8	
12	D₂O	70		100		
13	(CH₃)₃S=OI⁻[f,g]				26	35

[a] Isolated yields. [b] Determined by n.m.r. analysis. [e] Dimer (11) detected (t.l.c.) but not isolated. [d] Starting material (2b) detected (t.l.c.) but not isolated. [e] Prepared according to J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 3443. [f] Added as a solid (see H. Metzger, H. König, and K. Seelert, *Tetrahedron Letters*, 1964, 867; V. J. Traynelis and J. V. McSweeney, *J. Org. Chem.*, 1966, **31**, 243. [g] Reaction mixture heterogeneous (see E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353).

not affected by the addition of hexamethylphosphoramide (HMPA) even though it is known that HMPA selectivity solvates metal cations.[23] This observation is consistent with Still's conclusion[12] that, in the case of allylic anions, anion stabilizing groups result in less anion–counterion association. Involvement of (10) is therefore considered unlikely. We suggest that the anion has a W-configuration (6; R = C_6H_5), for steric reasons, and that this geometry persists in the transition state.

The major side-product occasionally formed in the reaction (Table 1) proved to be the α,γ-dimer (11). Since the yield increased when the purified solvent (THF) was stored before use, it is likely that the formation of the dimer (11) from the anion (6; R = C_6H_5) is catalysed by oxidising agents (*e.g.* peroxide) and involves a free radical mechanism. Although the oxidative coupling of dithian anions is known,[24] the coupling of keten thioacetalides has not been observed previously. The regioselectivity of the reaction is of particular note

(7) **(10)**

(11)
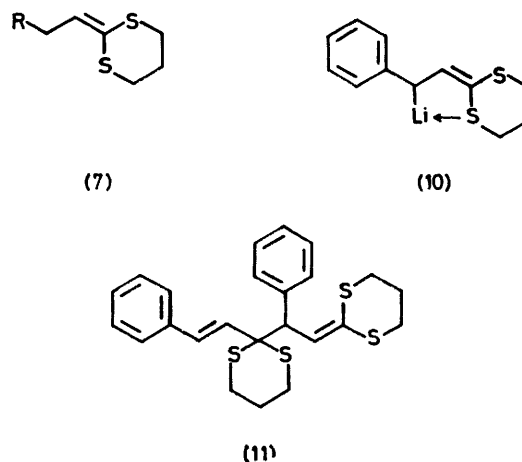
since the alkylation reactions (Table 1) indicate that the γ-position is less sterically hindered. On this basis γ–γ coupling would be anticipated. Further investigation will be required to establish the factors involved.

EXPERIMENTAL

M.p.s were obtained on a Thomas–Hoover m.p. apparatus and are uncorrected. T.l.c. was carried out on plates coated with silica gel HF$_{254}$ (Merck). Preparative layer chromatography (p.l.c.) on plates coated with Kieselgel PF$_{254}$ (Merck) were used. I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer as liquid films for liquids and as KBr discs for solids. ¹H N.m.r. spectra, unless otherwise stated, were obtained for solutions in deuteriochloroform with tetramethylsilane as an internal standard on a Perkin-Elmer R20A spectrometer.

Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl or lithium aluminium hydride under nitrogen. Light petroleum refers to that fraction of boiling range 40—60 °C.

Glassware, stirring pellets, and syringes used for the generation and reactions of lithium keten thioacetalides were dried at 110° overnight and allowed to cool under nitrogen.

2-(*Prop*-1-*enyl*)-1,3-*dithian* (2a).—To a solution of boron trifluoride–ether (2.4 ml) and glacial acetic acid (4.8 ml) in chloroform (10 ml) at refluxing temperature under nitrogen, was added a solution of freshly distilled crotonaldehyde (1.4 g, 0.022 mol) and propane-1,3-dithiol (2 ml, 0.02 mol) in chloroform (30 ml) at a constant rate over 6 h. The mixture was then allowed to cool to room temperature and washed successively with water, aqueous sodium hydroxide (10%), and water. The chloroform solution was dried (potassium carbonate) and concentrated *in vacuo* to give a brown oil. Chromatography on silica gel (ether–light petroleum, 1 : 9) gave a pale yellow oil of the *dithian* (2a) (1.45 g, 45%) (Found: C, 51.9; H, 7.5; S, 39.6 $C_7H_{12}S_2$ requires C, 52.4; H, 7.5; S, 40.0%); $\nu_{max.}$ 3 010, 2 900, 1 420, 1 270, 1 170, 1 040, 960, and 900 cm^{-1}; δ 1.85 (3 H, d, *J* 6 Hz, CH$_3$), 2.1 (2 H, m, CH$_2$), 2.85 (4 H, m, 2 × SCH$_2$), 4.55 (1 H, d, *J* 8 Hz, CHS$_2$), and 5.71 (2 H, m, vinylic protons).

2-(1-*Styryl*)-1,3-*dithian* (2b).[3,22]—*Method* (*a*).[6] To a solution of boron trifluoride–ether (2.4 ml) and glacial acetic acid (4.8 ml) in chloroform (8 ml) at refluxing temperature under nitrogen was added a solution of freshly distilled cinnamaldehyde (2.9 g, 0.022 mol) and propane-1,3-dithiol (2 ml, 0.02 mol) in chloroform (30 ml) at a constant rate over 6 h. The mixture was allowed to cool to room temperature and extractive work-up as described above gave a brown oil. Chromatography on silica gel (ether–light petroleum, 1 : 9) gave needles of the dithian (2b) (3.1 g, 70%), m.p. 57—58° (hexane) (Found: C, 64.7; H, 6.4; S, 28.6. Calc. for $C_{12}H_{14}S_2$: C, 64.8; H, 6.3; S, 28.8%); $\nu_{max.}$ 3 010, 2 900, 1 600, 1 500, 1 450, 1 420, 1 275, 1 215, 1 165, 960, 908, 760, and 690 cm^{-1}; δ 1.90 (2 H, m, CH$_2$), 2.75 (4 H, t, *J* 6 Hz, 2 × SCH$_2$), 4.65 (1 H, d, *J* 7 Hz, CHS$_2$), 6.8 (1 H, dd, *J* 7 and 16 Hz, PhCH=C*H*C), 6.75 (1 H, d, *J* 16 Hz, PhC*H*=CHC), and 7.30 (5 H, m, aromatic protons).

Method (*b*).[7] To a solution of cinnamaldehyde (2.64 g, 0.002 mol) and propane-1,3-dithiol (2.16 g, 0.002 mol) in dry ether (40 ml) at 0 °C under nitrogen was added boron trifluoride–ether (1.5 g, 0.001 mol) dropwise (10 min). The ice-bath was then removed and the mixture was stirred at room temperature for 3 h. The pale-yellow mixture was poured into aqueous sodium hydroxide (10%, 50 ml) and extracted with chloroform. The chloroform extracts were washed with water and brine, and dried (Na$_2$SO$_4$). Removal of the solvent *in vacuo* gave a pale yellow solid which was recrystallised from hexane to give a solid of (2b) (4.2 g, 95%) whose m.p. and t.l.c. and spectral properties were identical with the product from method a.

Preparation of 2-(m-*Methoxybenzyl*)-2-(*prop*-1-*enyl*)-1,3-*dithian* (3a).—To a solution of 2-(prop-1-enyl)-1,3-dithian (380 mg, 2.37 mmol) in THF (12 ml) at −40° under nitrogen was added n-butyl-lithium in n-hexane (1.8M, 1.4 ml, 2.49 mmol) and the mixture was stirred at −30 to −20°. After 1.5 h the orange solution was cooled to −40° and *m*-methoxybenzyl bromide [25] (476 mg, 2.37 mmol) in THF (4 ml) was added, forming a pale yellow solution. The mixture was stirred at −30 to −20° for 2 h and then warmed to room temperature over 2 h before being quenched with aqueous hydrochloric acid (1N). The mixture was extracted with chloroform. The combined chloroform extracts were washed with water and dried (Na$_2$SO$_4$). Solvent was removed *in vacuo* to give a pale yellow oil. P.l.c. (ether–light petroleum, 1 : 9) of crude oil afforded the *dithian* (3a) (332 mg, 50%) (Found: C, 64.3; H, 7.1; S, 22.7. $C_{15}H_{20}OS_2$ requires C, 64.4; H, 7.1; S, 22.9%); $\nu_{max.}$ 3 000, 2 910,

2 815, 1 600, 1 582, 1 490, 1 450, 1 260, 1 160, 1 050, 970, 910, 870, 780, and 600 cm^{-1}; δ 1.4—2.2 (5 H, m, CH$_2$ and CH$_3$), 2.4—3.2 (6 H, m, 2 × SCH$_2$ and ArCH$_2$), 3.77 (3 H, s, OCH$_3$), 5.55 (2 H, m, vinylic protons), and 6.5—7.3 (4 H, m, aromatic protons).

Hydrolysis of the Dithian (3a) *to give* 1-(m-*Methoxyphenyl*)-*pent*-3-*en*-2-*one* (1a).[8]—A solution of the dithian (3b) (200 mg, 0.71 mmol), methyl iodide (1 g, 7.1 mmol), and water (0.5 ml) in acetone (8 ml) was heated at reflux for 12 h. The solvent was removed *in vacuo* and the residue was diluted with water and extracted with ether. The ether extracts were washed with aqueous sodium hydrogen-carbonate (10%) and water, and dried (MgSO$_4$). Removal of the solvent *in vacuo* gave an oil which was purified by p.l.c. (ether–light petroleum, 1 : 9) to give the *enone* (1a) (88 mg, 65%) (Found: C, 76.0; H, 7.3. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%); $\nu_{max.}$ 1 680, 1 625, 1 600, and 1 580 cm^{-1}; δ 1.85 (3 H, d, *J* 6 Hz, CH$_3$), 3.66 (2 H, s, ArCH$_2$CO), 3.79 (3 H, s, OCH$_3$), 6.12 (1 H, d, *J* 16 Hz, CH=C*H*CO), and 6.61—7.46 (5 H, m, aromatic and vinylic protons).

General Method for the Preparation and Alkylation of Lithium Keten Thioacetalide (6; R = C_6H_5).—The solution of dithian (2b) (2.0 mmol) in dry THF (15 ml) was added and cooled to −40 °C (dry ice–acetone bath) under nitrogen. n-Butyl-lithium in hexane (1.8M, 2.1 mmol) was added slowly and the resulting dark orange solution was allowed to stir at −30 to −20° for 1 h. The mixture was then cooled to −40 °C and the alkylating agent (2.2 mol) in THF (5 ml) was added slowly by syringe, causing the highly coloured solution to fade to a pale yellow. The mixture was maintained at −30 to −20° for 2 h. The reaction was allowed to warm to room temperature (2 h) and quenched with aqueous hydrochloric acid (1N). The mixture was extracted with chloroform and the chloroform extracts were washed with water and dried (Na$_2$SO$_4$). Removal of the solvent *in vacuo* gave an oil which was analysed by t.l.c. and n.m.r. before being purified by p.l.c. (ether–light petroleum, 1 : 9) to afford the pure product.

With m-*methoxybenzyl bromide.* Treatment of *m*-methoxybenzyl bromide (442 mg, 2.2 mmol) with lithium keten thioacetalide (6; R = C_6H_5) prepared from the styryl-dithian (2b) (444 mg, 2.0 mmol) as described above gave after purification by p.l.c. a 1 : 9 mixture of the products (3b) and (4), respectively (n.m.r. analysis) as an oil (473 mg, 69%) (Found: C, 70.1; H, 6.6; S, 18.6. Calc. for $C_{20}H_{22}OS_2$: C, 70.1; H, 6.5; S, 18.7%); $\nu_{max.}$ 3 010, 2 910, 2 615, 1 600, 1 580, 1 490, 1 450, 1 260, 1 155, 1 040, 910, 875, 750, and 700 cm^{-1}; δ 2.05 (2 H, m, CH$_2$), 2.45—3.30 (6 H, m, 2 × SCH$_2$ and ArCH$_2$), 3.74 (3 H, s, OCH$_3$), 4.25 [m, PhCH of (4)], 5.9 [d, *J* 16 Hz, vinylic proton of (3b)], 6.0 [d, *J* 10 Hz, vinylic proton of (4)], and 6.50—7.50 (9 H, m, aromatic protons).

A mixture of the above product (274 mg, 0.8 mmol), mercury(II) chloride (432 mg, 1.6 mmol), mercury(II) oxide (172.8 mg, 0.8 mmol), water (1 ml), and acetone (5 ml) was heated at reflux under nitrogen for 3 h. T.l.c. showed one main spot of the product. The cooled mixture was filtered through Celite, and the solid was washed with acetone. Removal of the solvent *in vacuo* gave an oil which was diluted with water and extracted with dichloromethane. The dichloromethane extracts were washed with water and extracted with aqueous sodium hydrogencarbonate (10%). The aqueous layer was acidified with aqueous hydrochloric acid (10%) and extracted with ether. The ether extracts were washed with water and dried (MgSO$_4$). Removal of

TABLE 2

Products from the alkylation reactions of anion (6; $R = C_6H_5$)

Product	$\nu_{max.}/cm^{-1}$	Chemical shift (δ)	Found (%) [Calc. (%)]
(8 + 9; $R = C_6H_5CH_2$) oil	3 010, 2 900, 1 600, 1 580, 1 490, 1 450, 1 420, 1 275, 910, 750, 700	2.0 (2 H, m, CH_2), 2.69 (4 H, m, 2 × SCH_2), 2.98 (d, J 7.5 Hz, $PhCH_2$ of γ-isomer), 3.21 (s, $PhCH_2$ of α-isomer), 4.22 (m, PhCH of γ-isomer), 6.19 and 6.75 (q, AB system, J_{AB} 16 Hz, vinylic protons of α-isomer), 6.21 (d, J 10 Hz, vinylic protons of γ-isomer), and 7.25 (10 H, m, aromatic protons)	$C_{19}H_{20}S_2$ C, 72.9; H, 6.3; S, 20.2 (C, 73.0; H, 6.4; S, 20.5)
(11) m.p. 152—153 °C	3 010, 2 910, 1 600, 1 500, 1 420, 1 280, 1 220, 1 030, 980, 750, 700	2.0 (4 H, m, 2 × CH_2), 2.85 (8 H, m, 4 × SCH_2), 4.49 (1 H, d, J 10 Hz, PhCH), 6.24 and 6.88 (2 H, q, AB system, J_{AB} 16 Hz, PhCH=CHC), 6.51 (1 H, d, J 10 Hz, $CH=CS_2$), and 7.10—7.62 (10 H, m, aromatic protons)	$C_{24}H_{26}S_2$ C, 64.9; H, 5.9; S, 28.6 (C, 65.1; H, 5.8; S, 29.0) M.W. (ebullioscopic) 442 (442)
(8 + 9; $R = Pr^n$) oil	3 010, 2 900, 1 600 1 500, 1 450, 1 420, 1 270, 970, 740, 690	0.90 (3 H, t, J 6 Hz, CH_3), 1.15—2.40 (6 H, m, 3 × CH_2), 2.82 (4 H, m, 2 × SCH_2), 3.90 (m, PhCH of γ-isomer), 6.18 (d, J 10 Hz, vinylic proton of γ-isomer), 6.30 and 6.95 (q, AB system, J_{AB} 16 Hz, vinylic protons of α-isomer), and 7.49 (5 H, m, aromatic protons)	$C_{15}H_{20}S_2$ C, 68.4; H, 7.9; S, 24.0 (C, 68.2; H, 7.6; S, 24.2)
(8 + 9 $R = CH_3$) [22] oil	3 010, 2 910, 1 600, 1 580, 1 490, 1 440, 1 270, 1 150, 1 050, 960, 900, 750, 700	1.32 (d, J 7 Hz, CH_3 of γ-isomer), 1.69 (s, CH_3 of α-isomer), 2.0 (2 H, m, CH_2), 2.81 (4 H, m, 2 × SCH_2), 4.02 (dd J 7 and 10 Hz, PhCH of γ-isomer), 6.10 (d, J 10 Hz, vinylic proton of γ-isomer), 6.25 and 6.89 (q, AB system, J 16 Hz, vinylic protons of α-isomer), and 7.35 (5 H, m, aromatic protons)	$C_{13}H_{16}S_2$ C, 66.0; H, 6.7; S 27.0 (C, 66.1; H, 6.8; S 27.1)
(9; $R = CH_3$) oil	3 010, 2 900, 1 600, 1 580 1 485, 1 410, 1 270, 1 140, 1 060, 960, 910, 750, 700	1.69 (3 H, s, CH_3), 2.0 (2 H, m, CH_2), 2.81 (4 H, m, 2 × SCH_2), 6.25 and 6.89 (2 H, q, AB system, J 16 Hz, vinyl proton), and 7.35 (5 H, m, aromatic protons)	$C_{13}H_{16}S_2$ C, 66.2; H, 6.6; S, 27.0 (C, 66.1; H, 6.8; S, 27.1)
[9; $R = Si(CH_3)_3$] m.p. 100—101.5 °C	2 825, 1 440, 1 370 1 235, 910, 825, 720, 680	0.18 (9 H, s, 3 × CH_3), 2.0 (2 H, m, CH_2), 2.31 (1 H, m, SCH), 2.58 (1 H, t, J 3.8 Hz, SCH), 3.0 (2 H, m, SCH_2), 6.46 and 6.87 (2 H, q, AB system, J_{AB} 16 Hz, vinylic protons), and 7.49 (5 H, m, aromatic protons)	$C_{15}H_{21}S_2Si$ C, 60.9; H, 7.5; S, 21.7 (C, 61.4; H, 7.2; S, 21.8)

the solvent *in vacuo* gave an oil which was purified by p.l.c. (ether–light petroleum, 3 : 7) to give the 4-(m-*methoxyphenyl*)-3-*phenylbutyric acid* (5) (112 mg, 52%) (Found: C, 75.4; H, 6.4. $C_{17}H_{18}O_3$ requires C, 75.6; H, 6.6%); $\nu_{max.}$ 3 400—2 600 and 1 700 cm^{-1}; δ 2.65 (2 H, d, J 7.5 Hz, CH_2CO), 2.92 (2 H, d, J 7.5 Hz, $ArCH_2$), 3.35 (1 H, m, CH), 3.75 (3 H, s, OCH_3), and 6.5—7.4 (9 H, m, aromatic protons).

The alkylation of lithium keten thioacetalide (6; $R = C_6H_5$) with various alkylating agents was carried out according to the general method, and the $\alpha : \gamma$ ratio and the yield of the products are listed in Table 1. The physical properties and analytical data of the products are shown in Table 2.

With deuterium oxide. Treatment of the lithium thioacetalide prepared from the styryldithian (2b) as described above with excess of deuterium oxide (0.2 ml) gave an oil by the usual work-up. N.m.r. analysis showed no evidence of the formation of any of the γ-alkylation product (8; $R = D$). Purification by p.l.c. gave an oil of the α-alkylation product (9; $R = D$) (311 mg, 70%); δ 2.05 (2 H, m, CH_2), 2.90 (4 H, m, 2 × SCH_2), 6.30 and 6.85 (2 H, q AB system, J 16 Hz, vinylic protons), and 6.40 (5 H, m, aromatic protons).

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