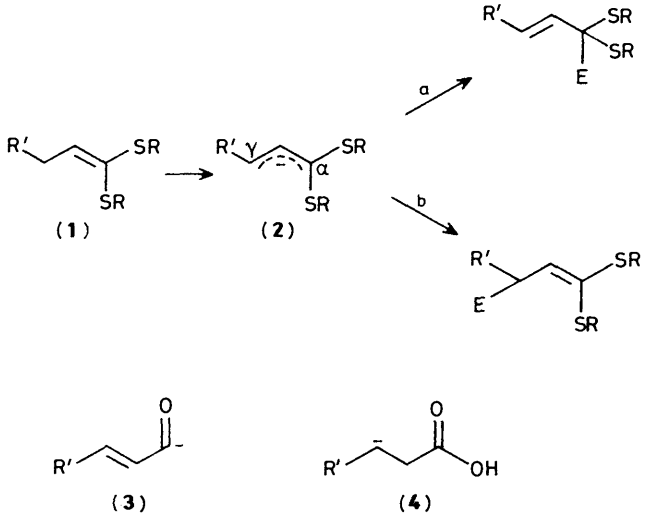
Synthesis and Reactivity of Lithiated γ-Functionalised Ketene Dithioacetals. Generation of a Flexible β-Lithioacrylate Equivalent

Edward Dziadulewicz, David Hodgson, and Timothy Gallagher*
School of Chemistry, Bath University, Bath, Avon BA2 7AY

The synthesis of 1,1,3-tris(phenylthio)prop-1-ene (**8**) is described. Anion (**9**), obtained by deprotonation of (**8**) with lithium di-isopropylamide, reacts with a wide range of electrophiles to give the γ-substituted adducts (**10**) exclusively. The relative importance of steric and electronic effects in determining the high γ-regioselectivity observed for (**9**) have been evaluated using a series of related ketene dithioacetals (**12**)—(**15**), and (**17**). The equivalence of anion (**9**) to a β-lithioacrylate has been illustrated by constructing a series of α,β-unsaturated γ- and δ-lactones and a short synthesis of (±)-eldanolide is also described. Anion (**9**) undergoes a facile dimerisation in the presence of oxygen to give dimer (**20**) and a mechanistic rationale for this observation is presented.

Ketene dithioacetals (**1**), which may be regarded as being synthetically equivalent to carboxylic acids, undergo facile deprotonation to give stabilised allylic anions (**2**). These ambident nucleophiles react with electrophiles at either the α-site, adjacent to both sulphur substituents, or at the other end of the allylic system, remote to sulphur, the γ-site (Scheme 1).[1]

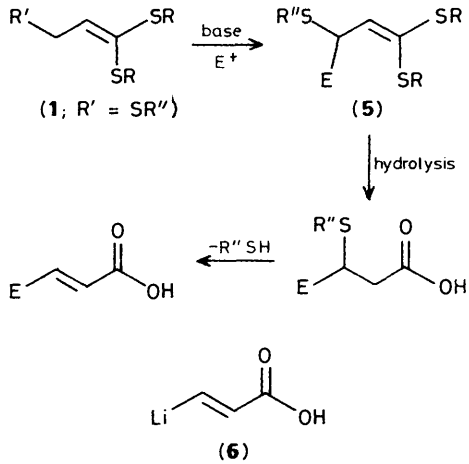


Scheme 1.

Various factors will influence this α/γ regioselectivity, not the least of which is the nature of the electrophilic component employed.[2] In general hard electrophiles (alkyl, allyl, silyl, halides) react at the α-site and soft electrophiles (aldehydes, some ketones) react predominantly at the γ-site. Ziegler *et al.* have shown that increasing the size of the substituent on sulphur tends to increase the proportion of the γ-adduct produced and the presence of co-solvents, as well as the nature of the counterion present, will also influence the regioselectivity observed.[3,4]

The reactivity shown in Scheme 1 should be considered in a broader context. By addition of an electrophile at the α-site (path a), anion (**2**) becomes equivalent to an acyl anion (**3**) and it is this mode of reactivity that has found most use in synthesis.[5] Anion (**2**) can also function as a homoenolate (**4**)[6] by reaction with electrophiles *via* the γ-site (path b). Although this mode of reactivity has not been widely exploited it does offer considerable potential provided that suitable conditions are available to promote high γ-regioselectivity for a wide range of both hard and soft electrophiles. It is, however, this lack of selectivity that at present limits the value of path b and a possible solution to this problem would be to incorporate an additional anion-stabilising substituent at the γ-site.[7] Murphy *et al.*[7b] have shown that the presence of an aryl residue [**1**; R/R = $(CH_2)_3$, R′ = Ph] does lead, for certain electrophiles, to a higher proportion of the γ-adduct. We felt that the introduction of an additional heteroatom, *e.g.* (**1**; R′ = SR″) would have a more pronounced effect on the α/γ regioselectivity for a wider range of electrophiles than had previously been observed.

The incorporation of this additional heteroatom has other implications beyond simply promoting high γ-regioselectivity (Scheme 2). Hydrolysis of the intact dithioacetal moiety present



Scheme 2.

in γ-adduct (**5**) would serve to release the latent carboxylate function. At this point the heteroatom substituent (SR″) becomes a potential leaving group and elimination of R″SH would generate the corresponding β-substituted acrylate. Thus (**2**; R′ = SR″) can also be regarded as equivalent to the lithio derivative (**6**), *i.e.*, a β-lithioacrylate. Since Caine's[8] early work on the halogen-metal exchange reactions of 3-bromopropenoic acid, a number of other synthetic equivalents of (**6**), based on either a stabilised vinyl or allyl anion, have appeared and the value of these reagents in synthetic chemistry is well established.[9–12]

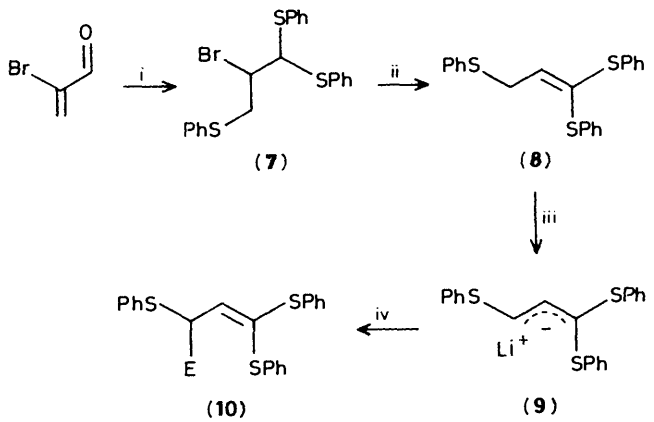
Table 1.

Electrophile	E in (**10**)	Yield (%)
Cyclopentanone	a; $C(OH)(CH_2)_3CH_2$	90
Cyclohexanone	b; $C(OH)(CH_2)_4CH_2$	93
1,2-Epoxyethane	c; $-CH_2CHOH$	72
Benzaldehyde	d; CH(OH)Ph	70*
MeI	e; Me	82
$BrCH_2CH{=}CH_2$	f; $-CH_2CH{=}CH_2$	82
$ClSiMe_3$	g; $SiMe_3$	95
$PhCH_2Br$	h; CH_2Ph	87
Me_2CHBr	i; Me_2CH	42
$BrCH_2CH_2CH{=}CH_2$	j; $-CH_2CH_2CH{=}CH_2$	74
$BrCH_2C{\equiv}CH$	k; $-CH_2C{\equiv}CH$	61
$ClCO_2Et$	l; CO_2Et	72

* 2:3 Mixture of diastereoisomers.

Results and Discussion

Our initial target was the γ-phenylthio derivative (**8**),[13] a reagent that combines both an anion-stabilising –SPh substituent with a high steric demand for the approach of an electrophile to the α-site. The preparation of (**8**) proceeded smoothly (Scheme 3). Addition of thiophenol (3 equiv.) to

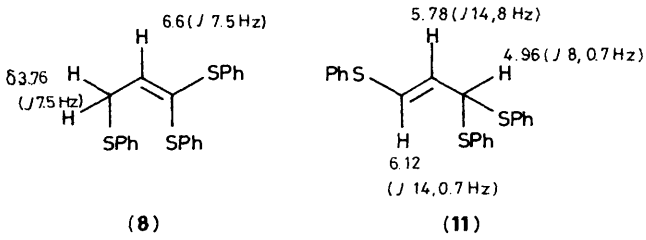


Scheme 3. *Reagents:* i, PhSH (3 equiv.), BF_3–Et_2O, CH_2Cl_2; ii, DBU, CH_2Cl_2; iii, LDA, THF, −78 °C to −40 °C; iv, E, THF, −78 °C

2-bromopropenal, in the presence of boron trifluoride–diethyl ether, gave adduct (**7**) which was used without further purification. Elimination of HBr from (**7**) was effected using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give the desired ketene dithioacetal (**8**) as a colourless oil which crystallised at low temperatures (< −5 °C). The overall yield of this procedure was 83% and this method has been used to prepare (**8**) on a 10—20 g scale.

Deprotonation of (**8**), using lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) solution, cleanly gave the corresponding allylic anion (**9**). This species reacted with a wide range of both hard and soft electrophiles and in all cases studied, the only product observed corresponded to the γ-adduct (**10**) (Table 1); no trace of an α-adduct was ever detected. ^1H N.m.r. spectroscopy was used to assign the structure (α versus γ) of the adducts obtained (*see below*) and these products, which tended to decompose on attempted distillation, were best purified by flash chromatography.

An alternative route is available to anion (**9**) which involves deprotonation of vinyl sulphide (**11**),[14] an isomer of ketene dithioacetal (**8**). Treatment of (**11**) with LDA generated anion (**9**) under essentially the same conditions as those used for (**8**). Addition of water to this solution of anion (**9**) gave only γ-adduct (**8**) with none of the α-adduct (**11**) being detected. These two isomers are readily distinguished by both t.l.c. and ^1H n.m.r. spectroscopy and the chemical shifts for (**8**) and (**11**), which were useful in confirming the structure of γ-adducts (**10**), are shown below.

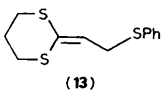
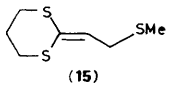
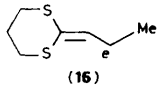
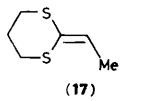


The very high γ-regioselectivity exhibited by (**9**) towards the broad spectrum of electrophiles shown in Table 1 is presumably due to a combination of factors. The high steric demands imposed at the α-site by the two –SPh residues would effectively shield this position from electrophilic attack. In addition, the γ-SPh substituent would be expected to exert an electronic perturbation that would favour electrophilic attack at the γ-site. In an attempt to understand the relative importance of these two factors we have examined a range of related ketene dithioacetals where the steric constraints operating at the α-site and the electronic influence of the γ-substituent have been varied. Ketene dithioacetals (**12**),[15] (**14**),[16] (**15**),[17] and (**17**)[18] were prepared by literature methods and (**13**)[19] was obtained in 55% yield by a modification of the method shown in Scheme 3, although no efforts were made to optimise this procedure. Deprotonation of (**12**)—(**15**) and (**17**) was carried out using the conditions described above for (**8**) and the resulting allylic anions were quenched with a representative series of electrophiles (trimethylsylyl chloride, benzyl bromide, and cyclohexanone). The product distribution (α- versus γ-adduct) for each substrate is shown in Table 2. Also included in this Table are relevant results from earlier studies, including those for the propylidene derivative (**16**).[20]

Several interesting points emerge from Table 2. Somewhat surprisingly, the nature of the electrophile (hard versus soft) does not have a dramatic effect on product distribution. The presence of hexamethylphosphoric triamide (HMPT), which can enhance α-selectivity,[20-23] similarly had little effect. Clearly the proportion of α-adduct increases as the α-site becomes more accessible to an incoming electrophile. This may either be achieved by decreasing the bulk of the substituent on sulphur or, as is the case with the dithianylidene systems, constraining the alkyl residues into a ring. The electronic effect of the γ-substituent is however more difficult to evaluate. This residue can exert an influence, but this situation is a more finely balanced one (entry 3 versus entry 5).

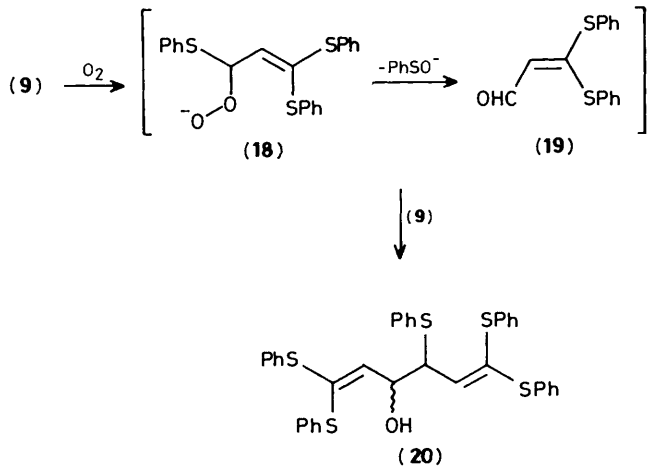
We therefore suggest that the high selectivity observed with anion (**9**) is primarily a consequence of the steric demands placed on the α-site.[24] The additional –SPh residue at the γ-site of (**9**) is not required to maintain this regioselectivity (*cf.* entry 1, Table 2) but the real value of this group lies in the synthetic flexibility that it imparts to the γ-substituted adducts (**10**), as outlined in Scheme 2, and this aspect of the chemistry of anion (**9**) is described in more detail below. The high regioselectivity exhibited by the anion derived from 1,1-bis(phenylthio)prop-1-ene (**12**) (entry 1, Table 2) is also worthy of note. This readily available ketene dithioacetal appears to provide a convenient, though as yet unexploited, equivalent to a homoenolate, $-CH_2CH_2CO_2R$.

Table 2.

Entry	Ketene dithioacetal	Electrophile: Me_3SiCl α:γ (% yield)	$PhCH_2Br$ α:γ (% yield)	Cyclohexanone α:γ (% yield)
1	$(PhS)_2C{=}CHMe$ (**12**)	0:100 (66)	0:100 (64)[a]	0:100 (75)
2	$(PhS)_2C{=}CHCH_2SPh$ (**8**)	0:100 (95)	0:100 (87)	0:100 (93)
3	 (**13**)	77:33 (44)	57:43 (44)[a]	60:40 (66)
4	$(MeS)_2C{=}CCH_2SMe$ (**14**)[b]	80:20 (35)	70:30 (46)	*c*
5	 (**15**)	100:0 (50)	100:0 (34)[a,d]	80:20 (45)
6	 (**16**)	100:0	*c*	82:18 (92)
7	 (**17**)	100:0 (87)[f]	100:0 (81)	85:15 (50)

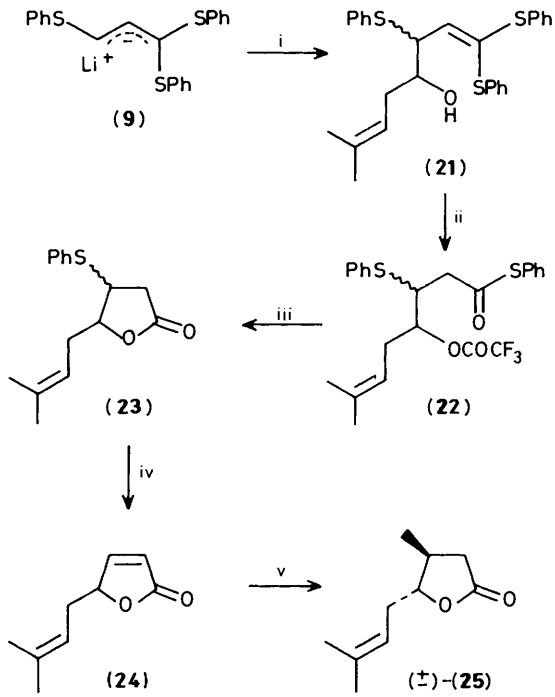
[a] When reaction was carried out in the presence of HMPT no significant change in the α:γ ratio was observed. [b] For related studies see reference 22 and also P. Breslin and A. Dlubala, *Tetrahedron Lett.*, 1986, **27**, 1687. [c] This combination was not studied. [d] A 94% yield has been reported together with the reaction of (**15**) with other electrophiles.[17] [e] Results shown in entry 6 are those of Fang, although no yield was reported for the reaction of (**16**) with $ClSiMe_3$.[20] See also F. E. Ziegler, U. P. Chakraborty, and R. T. Wester, *Tetrahedron Lett.*, 1982, **23**, 3237. [f] See reference 21.

Oxidative Dimerisation of Anion (**9**).[25]—In an attempt to formylate (**8**), a solution of anion (**9**) in THF containing dimethylformamide (DMF) was allowed to stand at −15 °C for 15 h. No formylated product adduct (**10**; E = CHO) was obtained, instead a 58% yield of a dimer, assigned as (**20**), was isolated. This material, which was present as a 4:3 mixture of diastereoisomers, was produced equally well in the absence of DMF and the source of the hydroxyl residue of (**20**) was established as molecular oxygen. When a methanol quench was used, no incorporation of a methoxy group was observed and dimerisation of (**9**), which was facile under an atmosphere of dry (CO_2-free)-air (61%, −78 °C, 1 h), was completely suppressed when oxygen was rigorously excluded. Although the usual spectroscopic techniques were used to characterise (**20**), satisfactory microanalytical data could not be obtained and the structure of (**20**) was confirmed by an independent synthesis. Reaction of the known aldehyde (**19**)[26] with (**9**) at −78 °C gave (**20**) in 82% yield, isolated as 1:1 mixture of diastereoisomers. We believe that this reaction plays a key role in the oxidative dimerisation of (**9**) and a reasonable rationale of this process is shown in Scheme 4. Oxidation of anion (**9**) with oxygen, presumably *via* an electron-transfer process, would lead to a peroxy intermediate (**18**).[27] Collapse of this species with elimination of $PhSO^-$ ($PhSH$ is not produced during the dimerisation reaction) would generate aldehyde (**19**) which reacts with another equivalent of anion (**9**) to give the oxidative dimer (**20**).



Scheme 4.

Use of Anion (**9**) *as a β-Lithioacrylate Equivalent.*—(−)-Eldanolide (**25**) is an agronomically important C-10 lactone isolated from the wing glands of the male African sugar cane borer, *Eldana saccharina*.[28] Eldanolide has been used[29] extensively as a vehicle for testing new synthetic methodology and the utility of reagent (**8**) has been illustrated by a short synthesis of (**25**), albeit in racemic form (Scheme 5).

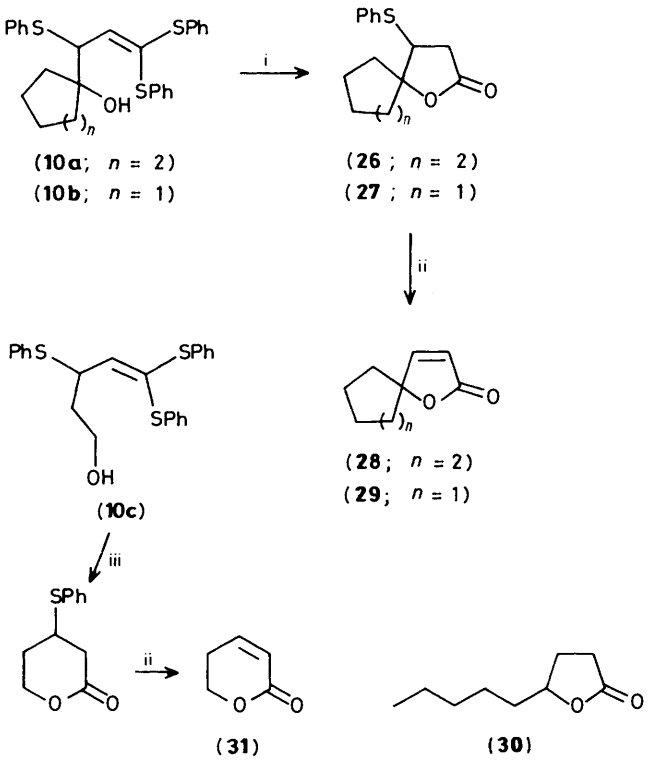


Scheme 5. *Reagents:* i, $Me_2C{=}CH_2CHO$, THF, −78 °C; ii, CF_3CO_2H, CH_2Cl_2; iii, $NaHCO_3$, MeOH; iv, DBU, CH_2Cl_2; v, ref. 28*c*

Addition of 4-methylpent-2-enal[30] to a solution of anion (**9**) gave the γ-adduct (**21**), as a 3:2 mixture of diastereoisomers in 85% yield. Attempts to effect the hydrolysis[31] of the ketene dithioacetal of (**21**), using aqueous acid or methods based on thiophiles such as mercury(II) in aqueous acetonitrile or aqueous tetrahydrofuran, were unsuccessful. However reaction of (**21**) with trifluoroacetic acid (9 equiv.) in dichloromethane[32] produced a single product that has been assigned as (**22**)

[$\nu_{max.}(CHCl_3)$ 1 780 ($OCOCF_3$), and 1 695 cm^{-1} (COSPh); M^+, 468]. Clearly rapid formation of a trifluoroacetyl ester has prevented lactone formation but this did not present a problem as (**22**) was smoothly converted, on treatment with sodium hydrogen carbonate in methanol, into lactone (**23**) [$\nu_{max.}(CHCl_3)$ 1 780 cm^{-1}] in 63% yield from (**21**). Elimination of thiophenol from (**23**) was achieved using DBU to give the known butenolide (**24**) in 45% yield. This material has been used as an intermediate in several syntheses of both racemic and optically pure eldanolide and our synthesis of (±)-(**25**) was completed by a stereoselective addition of lithium dimethyl cuprate to (**24**) in 60% yield using the conditions described by Kunesch.[28c]

This chemistry has been extended to adducts (**10a**) and (**10b**), derived from cyclohexanone and cyclopentanone respectively (Scheme 6). Acidic hydrolysis of these ketene dithioacetals at



Scheme 6. *Reagents:* i, CF_3CO_2H, CH_2Cl_2, −15 °C; ii, DBU, CH_2Cl_2; iii, CF_3CO_2H, CH_2Cl_2, room temperature

room temperature was accompanied by products resulting from competitive elimination of water. However, when this reaction was carried out at −15 °C, followed by addition of sodium hydrogen carbonate, the spirolactones (**26**) and (**27**) were formed more cleanly and following elimination of thiophenol, the spirobutenolides (**28**)[33] and (**29**)[33a] were isolated in 49% and 55% yield from (**10a**) and (**10b**) respectively.

Cyclisation of *e.g.*, (**10b**) to give lactone (**27**) may also be achieved using a weaker acid, such as acetic acid, and although the yield of this reaction is essentially quantitative, the reaction time at ambient temperature is increased to 6 weeks! Interestingly these spirobutenolides possess pleasant olfactory properties, both smelling strongly of coconut *cf.* γ-pelargonolactone (**30**), a known flavour component of coconut.[34]

The application of anion (**9**) to the synthesis of δ-lactones has also been briefly examined. Cyclisation of (**10c**), derived from ethylene oxide, followed by treatment with DBU using the conditions described above, gave 5,6-dihydropyran-2-one (**31**) in a moderate 35% overall yield.

In summary, the readily available γ-functionalised ketene dithioacetal (**8**) provides access to a sulphur-stabilised allylic anion (**9**) which functions effectively as a β-lithioacrylate equivalent. Although to date the use of this reagent has been limited to the synthesis of α,β-unsaturated lactones, we are continuing to develop its synthetic potential to encompass more highly functionalised heterocycles.

Experimental

All solvents and reagents were purified and dried by standard methods. Light petroleum refers to that fraction boiling in the range 60—80 °C. M.p.s were determined with a Gallenkamp melting point apparatus and are uncorrected. Chromatographic separations were performed using Merck Kieselgel 60 (Art 9385) or Merck Kieselgel 60H (Art 7736). I.r. spectra were recorded on either a Perkin-Elmer 197 or 1310 spectrometer. N.m.r. spectra were determined at 60 MHz on a Perkin-Elmer R-24B, at 100 MHz on a JEOL PS100 and at 270 MHz on a JEOL GX270 using tetramethylsilane as internal standard in deuteriochloroform. Mass spectra, electron impact (e.i.), and chemical ionisation (c.i.) using isobutane as the reagent gas, as well as high resolution mass determinations (e.i. only) were recorded on a VG Analytical 707E instrument with a VG 2000 data system. Elemental microanalyses were carried out using a Carlo Erba 1106 Elemental Analyser at Bath University.

Experimental details for reactions shown in Table 2 are available as supplementary data.*

1,1,3-*Tris(phenylthio)prop*-1-*ene* (**8**).—Thiophenol (9.96 g, 9.28 ml, 90.4 mmol) was slowly added to a solution of 2-bromopropenal (4.0 g, 29.7 mmol) in dichloromethane (70 ml) at room temperature. After 10 min BF_3–Et_2O (freshly distilled, 1.92 ml, 15.6 mmol) was added and the mixture was stirred for an additional 30 min before being poured into 10% aqueous sodium hydroxide (100 ml). The organic layer was separated, washed with 10% aqueous sodium hydroxide (5 × 100 ml) followed by brine (100 ml), and dried ($MgSO_4$). After removal of the drying agent by filtration, this solution containing 2-bromo-1,1,3-tris(phenylthio)propane (**7**) was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (4.6 g, 4.5 ml, 30 mmol). After 30 min the mixture was poured into 0.5M hydrochloric acid (100 ml) and the organic layer was separated, washed with water (30 ml), dried ($NaSO_4$), and concentrated under reduced pressure. Purification of the residue by flash chromatography gave, on elution with light petroleum, the *ketene dithioacetal* (**8**) as a colourless oil (8.9 g, 83%) (Found: M^+ − SPh, 257.044. $C_{15}H_{13}S_2$ requires M, 257.041); $\nu_{max.}$(thin film) 1 575 cm^{-1}; δ_H(60 MHz) 3.76 (2 H, d, J 7.5 Hz), 6.06 (1 H, t, J 7.5 Hz), and 6.70—7.30 (15 H, m); *m/z* (e.i.) 257 (M^+ − SPh, 100). Attempts to purify this material by distillation at reduced pressure resulted in extensive decomposition.

General Procedure for the Lithiation of (**8**) *and Reaction of Anion* (**9**) *with Electrophiles* (*Table 1*).—A solution of lithium diisopropylamide (LDA) [prepared from butyl-lithium (0.69 ml, 1.1 mmol; 1.6M in hexane) and di-isopropylamine (0.196 ml, 1.4 mmol)] in THF (3 ml) was cooled to −78 °C and a solution of ketene dithioacetal (**8**) (366 mg, 1 mmol) in THF (3 ml) was added dropwise. The resulting dark green solution was warmed to −40 °C over 1.5 h and maintained at this temperature for 30 min. After this time the solution of anion (**9**) was recooled to −78 °C and a solution of the electrophilic component (1.1 equiv.) in THF was added. The reaction mixtures were,

* Supplementary Publication No. 56726 (5 pages). For details see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1989, Issue 1.

with the exception of those involving an aldehyde or ketone, allowed to warm to room temperature before being quenched with saturated aqueous ammonium chloride (3 ml); reactions involving aldehydes or ketones were quenched at −78 °C. Water (25 ml) was then added and the mixture extracted with ethyl acetate (3 × 25 ml). The organic extracts were washed with brine (10 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The products were best purified by flash chromatography and were, unless otherwise stated, obtained as viscous oils.

1-[1,3,3-*Tris*(*phenylthio*)*prop*-2-*enyl*]*cyclopentanol* (**10a**). Prepared from cyclopentanone, (**10a**) (90%) (Found: M^+ − SPh, 341.105. $C_{20}H_{21}OS_2$ requires *M*, 341.103); $\nu_{max.}$(thin film) 3 450 and 1 580 cm^{-1}; δ_H (100 MHz) 1.47—2.00 (8 H, m), 2.32 (1 H, s, OH, exchanges with D_2O), 4.64 (1 H, d, *J* 10 Hz), and 6.75—7.65 (15 H, m); *m*/*z* (e.i.) 365 ($M^+ - C_5H_9O$, 2), 341 (M^+ − SPh, 80), and 77 (100).

1-[1,3,3-*Tris*(*phenylthio*)*prop*-2-*enyl*]*cyclohexanol* (**10b**). Prepared from cyclohexanone, (**10b**) (93%) (Found: C, 69.5; 6.21. $C_{27}H_{28}OS_3$ requires C, 69.8; H, 6.07%); $\nu_{max.}$(thin film) 3 450 and 1 580 cm^{-1}; δ_H(100 MHz) 1.18—1.90 (10 H, m,), 2.15 (1 H, s, OH exchanges with D_2O), 4.57 (1 H, d, *J* 10 Hz), 6.33 (1 H, d, *J* 10 Hz), and 6.68—7.55 (15 H, m), *m*/*z* (c.i.) 447 (M^+ − OH, 6), 366 (M^+ − SPh, 65), and 111 (100).

3,5,5-*Tris*(*phenylthio*)*pent*-4-*en*-1-*ol* (**10c**). Prepared from ethylene oxide, (**10c**) (72%) (Found: C, 67.2; H, 5.52. $C_{23}H_{22}OS_3$ requires C, 67.30; H, 5.40%); $\nu_{max.}$(thin film) 3 410 and 1 580 cm^{-1}; δ_H(100 MHz) 1.76—2.10 (3 H, m, containing OH), 3.70 (2 H, m), 4.67 (1 H, m), 6.04 (1 H, d, *J* 10 Hz), and 6.78—7.56 (15 H, m); *m*/*z* (c.i.) 411 (M^+ + 1, 3) and 301 (M^+ − SPh, 100).

α-[1,3,3-*Tris*(*phenylthio*)*prop*-2-*enyl*]*benzenemethanol* (**10d**). Prepared from benzaldehyde, (**10d**) (70%), 1:1 mixture of diastereoisomers. The two diastereoisomers were separated by flash chromatography. Isomer (i) R_F 0.36 (ethyl acetate–hexane, 1:9) (Found: C, 70.9; H, 5.5. $C_{28}H_{24}OS_3$ requires C, 71.15; H, 5.12%); $\nu_{max.}$(thin film) 3 480 and 1 580 cm^{-1}; δ_H (100 MHz) 2.76 (1 H, s, OH exchanges with D_2O), 4.67—4.94 (2 H, m), 6.22 (1 H, d, *J* 10 Hz), and 6.48—7.67 (20 H, m); *m*/*z* (c.i.) 455 (M^+ − OH, 9), 363 (M^+ − SPh, 42), and 111 (100). Isomer (ii) R_F 0.29 (ethyl acetate-hexane, 1:9) (Found: C, 71.0; H, 5.37. $C_{28}H_{24}OS_3$ requires C, 71.15; H, 5.12%); $\nu_{max.}$(thin film) 3 480 and 1 580 cm^{-1}; δ_H(100 MHz) 3.26 (1 H, s, OH exchanges with D_2O), 4.40—4.80 (2 H, m), 5.83 (1 H, d, *J* 9 Hz), and 6.45—7.60 (20 H, m); *m*/*z* (c.i.) 455 (M^+ − OH, 9), 363 (M^+ − SPh, 90), and 111 (100).

1,1,3-*Tris*(*phenylthio*)*but*-1-*ene* (**10e**). Prepared from either iodomethane or dimethylsulphate, (**10e**) (82%) (Found: M^+ − SPh, 271.060. $C_{16}H_{15}S_2$ requires *M*, 271.061); $\nu_{max.}$(thin film) 1 580 cm^{-1}; δ_H(100 MHz), 1.32 (3 H, d, *J* 7 Hz), 4.60 (1 H, m), 6.11 (1 H, d, *J* 10 Hz), and 6.88—7.55 (15 H, m); *m*/*z* (e.i.) 271 (M^+ − SPh, 100).

1,1,3-*Tris*(*phenylthio*)*hexa*-1,5-*diene* (**10f**). Prepared from 3-bromopropene, (**10f**) (82%) (Found: M^+ − SPh, 297.079. $C_{18}H_{17}S_2$ requires *M*, 297.077); $\nu_{max.}$(thin film) 1 640 and 1 580 cm^{-1}; δ_H(100 MHz) 2.12—2.70 (2 H, m), 4.58 (1 H, m), 4.90—5.20 (2 H, m), 5.75 (1 H, m), 6.08 (1 H, d, *J* 10 Hz), and 6.85—7.60 (15 H, m); *m*/*z* (e.i.) 365 ($M^+ - C_3H_5$, 1) and 297 (M^+ − SPh, 100).

Trimethyl[1,1,3-*tris*(*phenylthio*)*prop*-2-*enyl*]*silane* (**10g**). Prepared from chlorotrimethylsilane, (**10g**) (95%) (Found: M^+, 438.090. $C_{24}H_{26}S_3Si$ requires *M*, 438.096); $\nu_{max.}$(thin film) 1 575 cm^{-1}; δ_H(100 MHz) 0.20 (9 H, s), 4.16 (1 H, d, *J* 10 Hz), 6.32 (1 H, d, *J* 10 Hz), and 6.75—7.50 (15 H, m); *m*/*z* (e.i.) 438 (M^+, 1.5) and 329 (M^+ − SPh, 100).

4-*Phenyl*-1,1,3-*tris*(*phenylthio*)*but*-1-*ene* (**10h**). Prepared from benzyl bromide, (**10h**) (87%) (Found: C, 73.6; H, 5.3. $C_{28}H_{24}S_3$ requires C, 73.3; H, 5.42%); $\nu_{max.}$(thin film) 1 580 cm^{-1}; δ_H(100 MHz) 2.72 (1 H, dd, *J* 13 and 10 Hz), 3.31 (1 H, dd, *J* 13 and 5 Hz), 4.77 (1 H, td, *J* 10 and 5 Hz), 6.04 (1 H, d, *J* 10 Hz), and 6.40—7.55 (20 H, m); *m*/*z* (c.i.) 347 (M^+ − SPh, 100).

4-*Methyl*-1,1,3-*tris*(*phenylthio*)*pent*-1-*ene* (**10i**). Prepared from 2-bromopropane (**10i**) (42%) (Found: M^+ − SPh, 299.093. $C_{18}H_{19}S_2$ requires *M*, 299.093); $\nu_{max.}$(thin film) 1 580 cm^{-1}; δ_H(60 MHz) 1.03 (3 H, d, *J* 7 Hz), 1.12 (3 H, d, *J* 7 Hz), 2.00 (1 H, m), 4.37 (1 H, dd, *J* 10 and 6 Hz), 6.20 (1 H, d, *J* 10 Hz), and 6.70—7.70 (15 H, m); *m*/*z* (e.i.) 299 (M^+ − SPh, 100).

1,1,3-*Tris*(*phenylthio*)*hepta*-1,6-*diene* (**10j**). Prepared from 4-bromobut-1-ene, (**10j**) (74%) (Found: C, 71.2; H, 5.71. $C_{25}H_{24}S_3$ requires C, 71.4; H, 5.75%); $\nu_{max.}$(thin film) 1 640 and 1 580 cm^{-1}; δ_H(100 MHz) 1.50—2.33 (4 H, m), 4.52 (1 H, m), 4.80—5.17 (2 H, m), 5.67 (1 H, m) 6.05 (1 H, d, *J* 10 Hz), and 6.80—7.55 (15 H, m); *m*/*z* (c.i.) 421 (M^+ + 1, 5) and 311 (M^+ − SPh, 100).

4,6,6-*Tris*(*phenylthio*)*hex*-5-*en*-1-*yne* (**10k**). Prepared from 3-bromopropyne, (**10k**) (61%), m.p. 57—58 °C (from hexane) (Found: C, 71.2; H, 4.93. $C_{24}H_{20}S_3$ requires C, 71.24; H, 4.98%); $\nu_{max.}$(Nujol) 3 330 cm^{-1}; δ_H(100 MHz, $CDCl_3$) 2.06 (1 H, m), 2.58 (2 H, m), 4.56 (1 H, m), 6.16 (1 H, d, *J* 10 Hz), and 7.00—7.60 (15 H, m); *m*/*z* (c.i.) 405 (M^+ + 1, 1), 365 ($M^+ - CH_2CCH$, 1), and 295 (M^+ − SPh).

Ethyl 2,4,4-*tris*(*phenylthio*)*but*-3-*enoate* (**10l**). Prepared from ethyl chloroformate, (**10l**) (72%) (Found: M^+ − SPh, 329.062. $C_{18}H_{17}O_2S_2$ requires *M*, 329.062); $\nu_{max.}$(thin film) 1 730 and 1 580 cm^{-1}; δ_H(100 MHz) 1.18 (3 H, t, *J* 7 Hz), 4.12 (2 H, *q*, *J* 7 Hz), 5.18 (1 H, d, *J* 10 Hz), 6.22 (1 H, d, *J* 1.0 Hz), and 7.00—7.60 (15 H, m); *m*/*z* (e.i.) 295 (M^+ − SPh, 100).

2-[2-(*Phenylthio*)*ethylidene*]-1,3-*dithiane* (**13**). Thiophenol (800 mg, 0.76 ml, 7.42 mmol) was slowly added to an ice-cold stirred solution of 2-bromopropenal (1.0 g, 7.42 mmol) in dichloromethane (40 ml). After 10 min, BF_3–Et_2O (freshly distilled, 0.5 ml, 3.72 mmol) was added followed, after 10 min, by propane-1,3-dithiol (800 mg, 0.74 ml, 7.42 mmol). The mixture was stirred for a further 10 min then poured into 10% aqueous sodium hydroxide (50 ml). The organic layer was separated, washed with 10% aqueous sodium hydroxide (2 × 50 ml) and water (50 ml), and dried (Na_2SO_4). After removal of the drying agent by filtration this solution was treated with DBU (1.1 ml, 7.4 mmol). After 20 min the mixture was poured into 0.5M hydrochloric acid (50 ml), the organic layer was separated, washed with water, and dried (Na_2SO_4). After removal of the solvent, the orange residue was purified by flash chromatography to give the ketene dithioacetal (**13**) as a pale yellow oil (1.03 g, 55%) (Found: M^+ − SPh, 145.015. $C_6H_9S_2$ requires 145.014); $\nu_{max.}$(thin film) 1 580, 1 275, and 905 cm^{-1}; δ_H(60 MHz) 2.15 (2 H, m) 2.50—3.00 (4 H, m), 3.68 (2 H, d, *J* 8 Hz), 5.95 (1 H, t, *J* 8 Hz), and 7.00—7.55 (5 H, m); *m*/*z* (e.i.) 145 (M^+ − SPh, 100).

1,1,4,6,6-*Pentakis*(*phenylthio*)*hexa*-1,5-*dien*-3-*ol* (**20**).—A solution of anion (**9**), prepared as described above from ketene dithioacetal (**8**) (183 mg, 0.5 mmol) in THF (3 ml) was allowed to stand at −15 °C in a refrigerator for 15 h, after which time no trace of (**8**) was observed by t.l.c. The red solution was quenched with saturated aqueous ammonium chloride (2 ml) and water (25 ml) was added. The mixture was extracted with dichloromethane (2 × 25 ml) and the combined extracts were dried (Na_2SO_4), concentrated, and the residue was purified by flash chromatography to give *oxidative dimer* (**20**) as a pale yellow oil (105 mg, 58% as a 4:3 mixture of diastereoisomers), $\nu_{max.}$(thin film) 3 430br and 1 580 cm^{-1}. The two diastereoisomers could not be separated but for clarity, the ^1H n.m.r. data of the isomers are presented separately. Major isomer: δ_H(270 MHz) 2.82 (1 H, d, *J* 3 Hz, OH exchanges with D_2O), 4.57 [1 H, dd, *J* 10 and 9 Hz, $(PhS)_2C{=}CHCHSPh$], 4.87 [1 H, td, *J* 9 and 3 Hz, $(PhS)_2C{=}CHCHOH$], 5.96 [1 H, d, *J* 10 Hz,

$(PhS)_2C{=}CHCHSPh$], 6.01 [1 H, d, *J* 9 Hz, $(PhS)_2C{=}CHOH$], and 6.90—7.50 (25 H, m, ArH).

Minor isomer: δ_H(270 MHz) 2.45 (1 H, d, *J* 3 Hz, OH exchanged with D_2O), 4.57 [1 H, dd, *J* 10 and 9 Hz, $(PhS)_2C{=}CHCHSPh$], 4.87 [1 H, td, *J* 9 and 3 Hz, $(PhS)_2C{=}CHCHOH$], 5.96 [1 H, d, *J* 10 Hz, $(PhS)_2C{=}CHCHSPh$], 6.01 [1 H, d, *J* 9 Hz, $(PhS)_2C{=}CHCHOH$], and 6.90—7.50 (25 H, m, ArH); *m/z* (e.i.) 620 ($M^+ - H_2O$, 1.5), 527 (M^+ − SPh, 1), 512 (2), 407 (20), and 110 (PhSH, 100).

Synthesis of Oxidative Dimer (**20**) *from Anion* (**9**) *and* Aldehyde (**19**).—3,3-Bis(phenylthio)prop-2-enal (**19**) (243 mg, 0.89 mmol) in THF (2 ml) was added to a solution of anion (**9**) [from ketene dithioacetal (**8**) (336 mg, 0.92 mmol)] in THF at −78 °C. After 30 min at this temperature, saturated aqueous ammonium chloride (2 ml) was added, followed by water (25 ml). The mixture was extracted with dichloromethane (2 × 25 ml) and the combined extracts were dried (Na_2SO_4) and evaporated. Purification of the residue by flash chromatography gave compound (**20**) (466 mg, 82%, as a *ca.* 1:1 mixture of diastereoisomers). The chromatographic and spectroscopic properties of this material were identical with those described above.

7-*Methyl*-1,1,3-*tris*(*phenylthio*)*octa*-1,6-*dien*-4-*ol* (**21**).—Reaction of 4-methylpent-3-enal and 1,1,3-tris(phenylthio)-propene (**8**), under conditions that have previously been described, gave compound (**21**) in 85% yield as a 3:2 mixture of diastereoisomers which were not separated (Found: M^+ − SPh, 355.119. $C_{21}H_{23}OS_2$ requires *M*, 355.119); $\nu_{max.}$(thin film) 3 470 and 1 580 cm^{-1}; δ_H(100 MHz) 1.61 (6 H, s, major isomer), 1.71 (6 H, s, minor isomer), 2.12—2.50 (6 H, s, major isomer), 1.71 (6 H, s, minor isomer), 2.12—2.50 (6 H, m, contains both OH as judged by D_2O both isomers), 3.47—3.92 (1 H, m, both isomers), 4.44—4.73 (1 H, m, both isomers), 5.00—5.25 (1 H, m, both isomers), 6.07 (1 H, d, *J* 10 Hz, minor isomer), 6.32 (1 H, d, *J* 10 Hz, major isomer), and 6.90—7.60 (15 H, m, both isomers); *m/z* (c.i.) 465 (M^+ + 1, 1), 447 (M^+ − OH, 4), and 355 (M^+ − SPh, 100).

7-*Methyl*-3-*phenylthiooct*-6-*en*-4-*olide* (**23**).—Trifluoroacetic acid (0.88 ml, 10 mmol) was added to a stirred solution of (**21**) (530 mg, 1.1 mmol) in dichloromethane (10 ml) at room temperature. After 20 min water (8 ml) was added (strong odour of thiophenol!) and after mixing well the organic solution was separated and shaken with aqueous sodium hydrogen carbonate (2 × 15 ml) followed by water (15 ml). The organic layer was then dried (Na_2SO_4) and evaporated. The residue was redissolved in anhydrous methanol (5 ml), treated with sodium hydrogen carbonate (500 mg) and the mixture was stirred vigorously for 15 min. After this time water (10 ml) was added and the product was extracted with ethyl acetate (3 × 10 ml). The combined extracts were washed with water (10 ml), dried (Na_2SO_4),and concentrated. Purification of residue by flash chromatography gave lactone (**23**) (187 mg, 63%) as a mixture of diastereoisomers (Found: M^+, 262.102. $C_{15}H_{18}O_2S$ requires 262.103); $\nu_{max.}$($CHCl_3$) 1 780 cm^{-1}; δ_H(60 MHz) 1.55 (3 H, s) 1.67 (3 H, s), 2.20—2.50 (2 H, br t, *J* 7 Hz), 2.50—2.90 (2 H, dd, *J* 11 and 7 Hz), 3.57 (1 H, m), 4.33 (1 H, q, *J* 6 Hz), 5.01 (1 H, br t, *J* 7 Hz), and 7.20—7.50 (5 H, m); *m/z* (e.i.) 262 (M^+, 100) 234 (M^+ − CO, 29), and 152 (M^+ − PhSH, 20).

7-*Methylocta*-2,6-*dien*-4-*olide* (**24**).—DBU (0.14 ml, 0.93 mmol) was added to an ice-cold solution of (**23**) (222 mg, 0.85 mmol) in dichloromethane (10 ml). The mixture was stirred for 30 min, 1M hydrochloric acid (5 ml) was added, and the organic layer was separated, washed with 1M hydrochloric acid (10 ml) and water (10 ml), then dried (Na_2SO_4). Evaporation of the solvent and purification of the residue by flash chromatography gave butenolide (**24**) (58 mg, 45%). Spectroscopic data obtained from (**24**) were identical with those previously reported.[28a]

1-*Oxaspiro*[4.4]*non*-3-*en*-2-*one* (**29**).—Trifluoroacetic acid (0.11 ml, 1.4 mmol) was added to a stirred solution of (**10b**) (100 mg, 0.22 mmol) in dichloromethane (20 ml) at −15 °C. After 20 h at this temperature the green solution was poured into saturated aqueous sodium hydrogen carbonate (20 ml). The organic layer was separated, washed with saturated aqueous sodium hydrogen carbonate (3 × 20 ml), water (20 ml), and dried (Na_2SO_4). After removal of the drying agent by filtration, DBU (0.07 ml, 0.44 mmol) was added and after 1.5 h the solution was washed with 1M HCl (20 ml) and water (20 ml), and dried (Na_2SO_4). Evaporation of the solvent followed by filtration through silica gel gave 1-oxaspiro[4.4]non-3-en-2-one (**29**) (17 mg, 55%). Spectral data obtained for (**29**) were identical with those reported previously.[33a]

1-*Oxaspiro*[4.5]*dec*-3-*en*-2-*one* (**28**).—A stirred solution of compound (**10a**) was treated as described above for (**10b**) with trifluoroacetic acid followed by DBU to give 1-oxaspiro[4.5]-dec-3-en-2-one (**28**) (49%). The spectral data obtained for (**28**) were identical with those reported previously.[33]

5,6-*Dihydropyran*-2-*one* (**31**).—Trifluoroacetic acid (0.3 ml, 3.77 mmol) was added to a stirred solution of (**10c**) (238 mg, 0.58 mmol) in dichloromethane (10 ml) at room temperature. The solution rapidly became green changing over 20 min to dark red after which time water (3 ml) was added. This mixture was then washed with saturated aqueous sodium hydrogen carbonate (2 × 10 ml) and water (10 ml) and the organic layer was separated and dried (Na_2SO_4). After removal of the drying agent by filtration the solution was cooled to 0 °C and DBU (0.034 ml, 0.23 mmol) was added. After 10 min the solution was washed with 1M hydrochloric acid (3 ml) followed by water (5 ml) and dried (Na_2SO_4). Removal of the solvent followed by filtration through silica gel gave 5,6-dihydropyran-2-one (**31**) which was identical with an authentic sample.

Acknowledgements

We thank Professor M. A. McKervey and Dr. B. M. Dilworth (U. C. Cork) for generously providing the sample of (**11**) used in this study and the S.E.R.C. and Bath University for financial support.

References

1 (*a*) M. Kolb in 'The Chemistry of Ketenes, Allenes and Related Compounds,' ed. S. Patai, Wiley, New York, 1980, p. 670; (*b*) B. T. Gröbel and D. Seebach, *Synthesis*, 1980, 357.
2 (*a*) W. S. Murphy and S. Wattanasin, *Tetrahedron Lett.*, 1979, 1827; (*b*) A. P. Kozikowski and Y.-Y. Chen, *J. Org. Chem.*, 1980, **45**, 2236; (*c*) S. Hunig, N. Klaunzer, and R. Schlund, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1281.
3 (*a*) F. E. Ziegler and C. C. Tam, *J. Org. Chem.*, 1979, **44**, 3428; (*b*) T. Fujisawa, K. Umezu, M. Sukaki, and T. Sata, *Chem. Lett.*, 1986, 1675.
4 F. E. Ziegler, J.-M. Fang, and C. C. Tam, *J. Am. Chem. Soc., 1982*, **104**, 7174.
5 For a recent synthetic application see B. Lindgren, P. Stjernlof, and L. Trogen, *Acta Chem. Scand., Ser. B*, 1987, **41**, 180. See also D. Seebach, M. Kolb, and B. T. Gröbel, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 69. For other important uses of ketene dithioacetals see T. Cohen and R. B. Weisenfield, *J. Org. Chem.*, 1979, **44**, 3601.
6 For reviews of homoenolate equivalents see: (*a*) N. H. Werstiuk, *Tetrahedron*, 1983, **39**, 205; (*b*) J. C. Stowell, *Chem. Rev.*, 1984, **84**, 409; (*c*) D. Hoppe, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 932.
7 (*a*) A. I. Meyers and R. C. Strickland, *J. Org. Chem.*, 1972, **37**, 2579; (*b*) W. S. Murphy and S. Wattanasin, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2679.

8 D. Caine and A. S. Frobese, *Tetrahedron Lett.*, 1978, **19**, 5167.
9 D. Caine and V. C. Ukachukwu, *Tetrahedron Lett.*, 1983, **24**, 3959; D. Caine, A. S. Frobese, and V. C. Ukachukwu, *J. Org. Chem.*, 1983, **48**, 740; D. Caine and V. C. Ukachukwu, *J. Org. Chem.*, 1985, **50**, 2195.
10 K. Iwai, H. Kosugi, A. Miyazaki, and H. Uda, *Synth. Commun.*, 1976, **6**, 357; K. Isobe, M. Fuse, H. Kosugi, H. Hagiwara, and H. Uda, *Chem. Lett.*, 1979, 785.
11 R. R. Schmidt, *Bull. Soc. Chim. Belg.*, 1983, **92**, 825; N. C. Barua and R. R. Schmidt, *Synthesis*, 1986, 1067; see also reference 29*k*.
12 S. De Lombaert, I. Nemery, B. Roekens, J. C. Carretero, T. Kimmel, and L. Ghosez, *Tetrahedron Lett.*, 1986, **27**, 5099; S. Dehomaert, B. Lesur, and L. Ghosez, *ibid.*, 1982, **23**, 4251; S. K. Richardson, A. Jeganathan, and D. S. Watt, *ibid.*, 1987, **28**, 2335.
13 For a preliminary account of this work see E. Dziadulewicz and T. Gallagher, *Tetrahedron Lett.*, 1985, **26**, 4757.
14 J. P. Cronin, B. M. Dilworth, and M. A. McKervey, *Tetrahedron Lett.*, 1986, **27**, 757.
15 T. Cohen, R. E. Gapinski, and R. H. Hutchins, *J. Org. Chem.*, 1979, **44**, 3599.
16 P. Beslin and A. Dlubala, *Tetrahedron Lett.*, 1986, **27**, 1687.
17 E. J. Corey and A. P. Kozikowski, *Tetrahedron Lett.*, 1975, 925.
18 E. J. Corey and D. J. Beams, *J. Am. Chem. Soc.*, 1973, **95**, 5829.
19 Y. Nagao, K. Seno, and E. Fujita, *Tetrahedron Lett.*, 1979, 4403.
20 (*a*) J.-M. Fang, L.-F. Liao, and B.-C. Hong, *J. Org. Chem.*, 1986, **51**, 2828; (*b*) J.-M. Fang, B.-C. Hong, and L.-F. Liao, *ibid.*, 1987, **52**, 855.
21 N. H. Anderson, D. A. McCrae, D. B. Grotjahn, S. Y. Gabhe, L. J. Theodore, R. M. Ippolito, and T. K. Sarkar, *Tetrahedron*, 1984, **37**, 4069.
22 L. Hevesi, K. M. Nsunda, and M. Renard, *Bull. Soc. Chim. Belg.*, 1985, **94**, 1039.
23 P. M. Atlani, J. F. Biellmann, S. Dube, and V. V. Vicens, *Tetrahedron Lett.*, 1974, 2665.
24 For conjugate addition reactions involving (**9**) see: (*a*) T. Cohen, W. D. Abrahams, and M. J. Myers, *J. Am. Chem. Soc.*, 1987, **109**, 7923; (*b*) T. Cohen and M. Myers, *J. Org. Chem.*, 1988, **53**, 457.
25 The oxidative dimerisation of 2-lithio-1,3-dithianes has been reported. E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1986, **4**, 1077.
26 P. Freche, A. Gorgues, and E. Levas, *Tetrahedron*, 1977, **33**, 2069.
27 B. J. Wakefield, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 7, p. 63.
28 (*a*) G. Kunesch, P. Zagatt, J. Y. Lallemand, A. Debal, and J. P. Vigneron, *Tetrahedron Lett.*, 1981, **22**, 5271; (*b*) J. P. Vigneron, R. Meric, M. Larcheveque, A. Debal, G. Kunesch, P. Zagatti, and M. Gallois, *ibid.*, 1982, **23**, 5051; (*c*) J. P. Vigneron, R. Meric, M. Larcheveque, A. Debal, J. Y. Lallemand, G. Kunesch, P. Zagatti, and M. Gallons, *Tetrahedron*, 1984, **40**, 3521.
29 Syntheses of (+)- or (−)-(**9**): (*a*) K. Mori and Y. Umemura, *Tetrahedron Lett.*, 1982, **23**, 3391; (*b*) T. Uematsu, T. Umemura, and K. Mori, *Agric. Biol. Chem.*, 1983, **47**, 597; (*c*) Y. Yokoyama and M. Yuokihara, *Chem. Lett.*, 1983, 1245; (*d*) H. G. Davies, S. M. Roberts, B. J. Wakefield, and J. A. Winders, *J. Chem. Soc., Chem. Commun.*, 1985, 1166; (*e*) K. Suzuki, T. Ohkuma, and G. Tsuchihashi, *Tetrahedron Lett.*, 1985, **26**, 861; (*f*) R. M. Ortuno, R. Merce, and J. Font, *ibid.*, 1986, **27**, 2519; (*g*) D. S. Matteson, K. M. Sadhu, and M. L. Peterson, *J. Am. Chem. Soc.*, 1986, **108**, 810; see also ref. 7*c*. Syntheses of (±)-(**9**): (*h*) T. K. Charkaborty and S. Chandraseharan, *Tetrahedron Lett.*, 1984, **25**, 2891; (*i*) R. Iriye, *Agric. Biol. Chem.*, 1985, **49**, 2775; (*j*) H. Frauenrath and T. Phillips, *Tetrahedron*, 1986, **42**, 1135; (*k*) N. C. Barua and R. R. Schmidt, *Synthesis*, 1986, 891; (*l*) J.-M. Fang and B.-C. Hong, *Synth. Commun.*, 1986, **16**, 523; (*m*) J.-M. Fang, B.-C. Hong, and L.-F. Liao, *J. Org. Chem.*, 1987, **52**, 855; (*n*) C. W. Jefford, A. W. Sledeski, and J. Boukouvalas, *Tetrahedron Lett.*, 1987, **28**, 949.
30 M. Julia and G. Le Thuillier, *Bull. Soc. Chim. Fr.*, 1966, 717.
31 (*a*) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, 1970, **35**, 764; (*b*) E. J. Corey and D. J. Beames, *J. Am. Chem. Soc.*, 1973, **95**, 5829.
32 D. Seebach and R. Burstinghaus, *Synthesis*, 1975, 461.
33 (*a*) P. Canonne, D. Belanger, and G. Lemay, *J. Org. Chem.*, 1982, **47**, 3953; see also; (*b*) S. Torii, T. Okamoto, and H. Tanaka, *ibid.*, 1974, **39**, 2486; L. J. Haynes and E. R. H. Jones, *J. Chem. Soc.*, 1946, 954.
34 Y. Terai and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1956, **29**, 822.

Received 11*th April* 1988; *Paper* 8/01410H