Phenylthio Migrations in Rearrangements of 2,2-Bisphenylthioethanols

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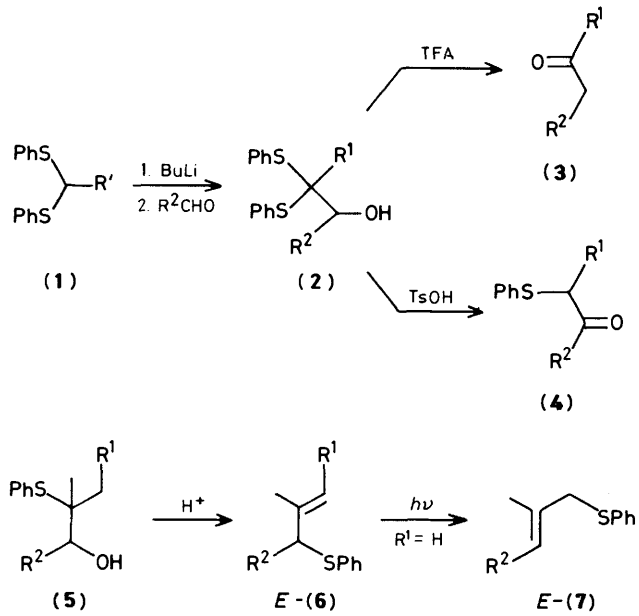
Thionyl chloride causes rearrangement of the title compounds to give 2,3-bisphenylthiopropenes (**12**) by a [1,2] phenylthio shift. The products undergo [1,3] phenylthio shifts on exposure to light. Some applications to synthesis are described.

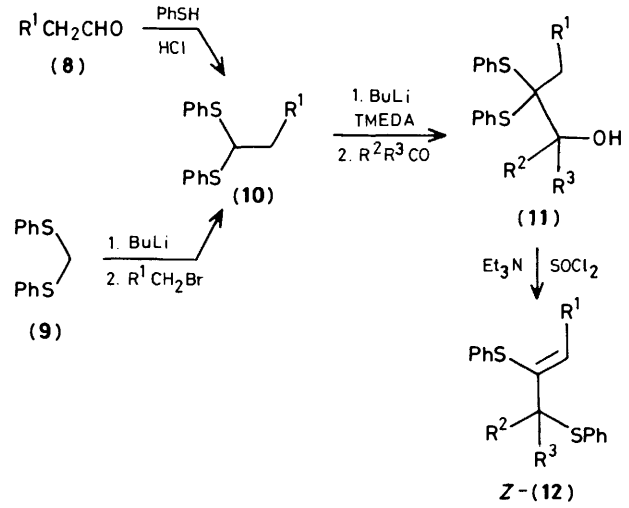
Adducts (**2**) from aldehydes and anions of bisphenylthio acetals (**1**) give ketones (**3**) on treatment with trifluoroacetic acid (TFA) and α-phenylthio ketones (**4**) with toluene-*p*-sulphonic acid (TsOH).[1] These useful reactions surprised us because compounds analogous to (**2**) but having only one phenylthio group (**5**) rearrange[2,3] in acid with phenylthio migration to give allyl sulphides (**6**). Photochemical [1,3] phenylthio shifts[4] on the products (**6**) to give allyl sulphides (**7**) with more substituents on the double bond, and the extension of these reactions to



molecules with other functional groups,[5] make available a range of substituted allyl sulphides. We now report that the bisphenylthio compounds (**2**) undergo similar [1,2] and [1,3] phenylthio shifts, though under different conditions (Scheme 1), and on some uses of the products in synthesis.[6]

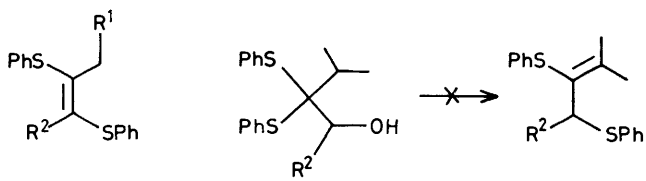
The bisphenylthio acetals (**10**) are accessible directly from aldehydes (**8**) or by alkylation of bisphenylthiomethane (**9**). The carbanion from (**10**) is best made[1] with n-butyl-lithium (BuLi) in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and adds to aldehydes or ketones to give adducts (**11**) in good yield (Table 1).

Attempts to rearrange adducts (**11**) to the allyl sulphides (**12**) had been thwarted by protonation at sulphur instead of at oxygen in the formation of α-phenylthio ketones or by hydrolysis of the allyl sulphides (**12**) during the formation of ketones (**3**).[1] We therefore turned to sulphonyl halides which would attack oxygen rather than sulphur and would maintain anhydrous conditions. Tosyl chloride and triethylamine gave no reaction. Thionyl chloride and pyridine or methanesulphonyl chloride and triethylamine gave some of the allyl sulphide (**12**)



Scheme 1.

with the ene disulphide (**13**) when R^3 = H. Finally we found that thionyl chloride and triethylamine in carbon tetrachloride at 0 °C for a few minutes in a foil-wrapped flask (to prevent subsequent [1,3] phenylthio shifts) gave excellent yields of the allyl sulphides (**12**) (Table 1).



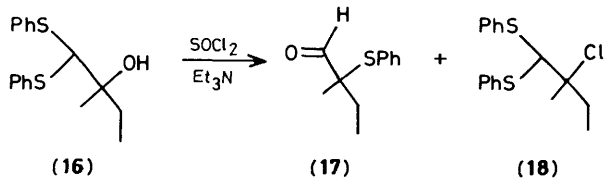
With a methyl group at the migration origin (R^1 = H: **11a**, **11b**, Table 1) or in aldehyde adducts (R^3 = H) when R^2 = Ar (**11b**, **11h**) the ene disulphide (**13**) was still the product, but in almost all other cases the reaction is rapid and high-yielding. The substituents may be methyl or primary alkyl, and ketone adducts with R^2 = Ph rearranged successfully. Complex mixtures of products which could not be separated were formed from formaldehyde adducts [R^2 = R^3 = H, *e.g.* (**11c**)], or when a secondary alkyl group replaces R^1CH_2 (**14**) so that the product (**15**) would have a tetra-substituted double bond (**11j**), (**11k**). However, good yields were obtained when R^1 was vinylic (**11l**), (**11m**) so that the developing double bond was conjugated (**12l**), (**12m**).

The rearrangement to allyl sulphides (**12**) is impossible for adducts (**16**) and (**19**). The tertiary alcohol (**16**) gave the α-phenylthio aldehyde (**17**) in 54% yield (by phenylthio migration) and the unrearranged chloride (**18**) in 36% yield. The

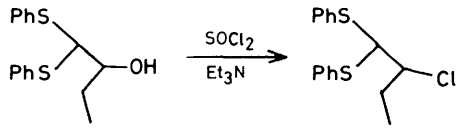
Table 1. Rearrangement of adducts (**11**) to substituted 2,3-bisphenylthioprop-1-enes (**12**)

	Starting materials					Products	
	Yield (%)	R^1	R^2	R^3		Yield (%)	Stereo *E*:*Z*
(**11a**)	52[a]	H	Me	H	(**13a**)	82	2:1
(**11b**)	57[a]	H	Ph	H	(**13b**)	99	1:1
(**11c**)	71	Me	H	H	*b*		
(**11d**)	73[a]	Me	Me	H	(**12d**)	90	1:1
(**11e**)	76[a]	Me	Et	H	(**12e**)	83	3:2
(**11f**)	59[a]	Me	n-C_6H_{13}	H	(**12f**)	96	3:2
(**11g**)	(100)[c]	Me	MeCH=CH	H	*b*		
(**11h**)	52[a]	Me	Ph	D	(**12h**)	*d*	
(**11i**)	62[a]	n-Pr	Me	H	(**12i**)	91	1:1
(**11j**)	59	Pr^i[e]	Et	H	*b*		
(**11k**)	72[a]	Pr^i[e]	Ph	H	*b*		
(**11l**)	52	CH=CH_2	Et	H	(**12l**)	(100)[c]	*E* only
(**11m**)	73	CMe=CH_2	Et	H	(**12m**)	(100)[c]	2:1
(**11n**)	64	Ph	Et	H	(**12n**)	(100)[c]	*E* only
(**11o**)	68[a]	Me	$[CH_2]_5$		(**12o**)	40[f]	3:2
(**11p**)	56[a]	Me	Me	CH_2Ph	(**12p**)	95	2:1
(**11q**)	80[a]	Et	Me	Ph	(**12q**)	80	3:2
(**11r**)	71[a]	Bu^i	Me	Me	(**12r**)	76	1:1

[a] See Ref. 1. [b] Mixture of products, see text. [c] Yield of crude product which decomposed on preparative layer chromatography. [d] 92% of a 2:1 mixture of (**12h**) and (**13h**). [e] R^1CH_2=Pr^i, see text. [f] From impure (**11o**), contains *ca.* 20% of the product of a [1,3]phenylthio shift.



(**16**) (**17**) (**18**)



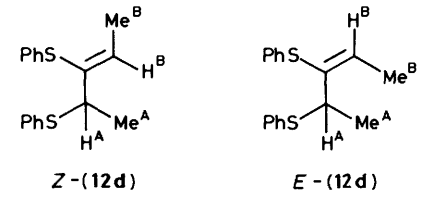
(**19**) (**20**)

corresponding chloride (**20**) was the only product we could isolate (26%) in the attempted rearrangement of the secondary alcohol (**19**).

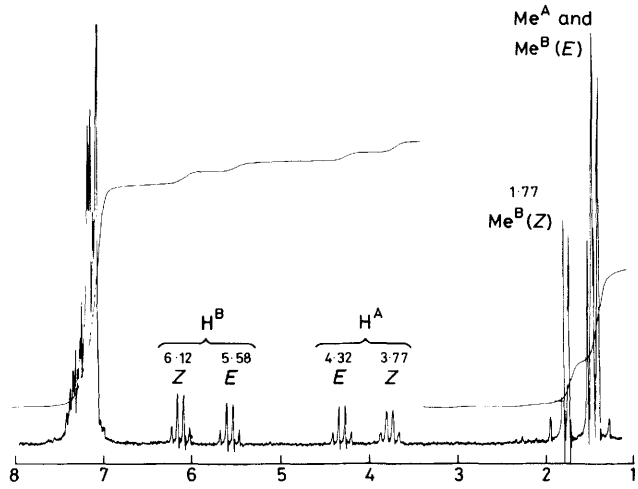
Assignment of Stereochemistry to the Rearranged Sulphides (**12**).—The phenylthio migration products (**12**) were mostly formed as mixtures of geometrical isomers, one (to which we assign the *E*-configuration) being favoured. In two cases (**12l**), (**12n**) the *E*-isomer was the only product. These isomers could not be separated but were easily identified (when R^3 = H) from the n.m.r. spectrum of the mixture as protons A (allylic) and B (vinylic) resonate at different chemical shifts for the two isomers, those for one isomer being outside those for the other (Figure).

Calculations[7] and observations[8] agree that for vinylic sulphides with trisubstituted double bonds (**21**) the vinyl proton in the *Z*-isomer (*i.e. trans* to *RS*) resonates at lower field than does the vinyl proton of the *E*-isomer.

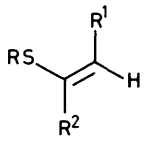
Analogies for the effect of the other sulphur atom are harder to find, but the n.m.r. spectra of the *E*- and *Z*-isomers of the allyl sulphides (**22**), which we prepared by rearrangement of (**5**; R^1 = Bu^i, R^2 = Me)[2], show that the PhSCHMe group has little effect on the relative shifts of the vinyl protons B which resonate at 5.20 in both isomers. However, the allylic proton PhSCH^AMe resonates at lower field in the *Z*-isomer (4.48) than in the *E*-isomer (3.78). The chemical shifts of the allylic protons A for all



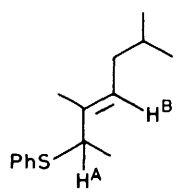
Z-(**12d**) *E*-(**12d**)



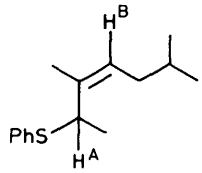
compounds (**12**) (Table 2) fall in the range δ 4.19—4.41 for one isomer, which we therefore assign the *E* configuration, and 3.65—3.85 for the other, assigned the *Z* configuration. The resonances of the vinyl protons B are further downfield than



Z-(**21**)



E-(**22**)



Z-(**22**)

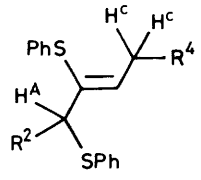
Table 2. Chemical shifts of the allylic and vinylic protons of the bisphenylthio compounds (**12**)

				Chemical shifts (p.p.m.)			
				Z-Isomer		*E*-Isomer	
Compound	R^1	R^2	R^3	H^A	H^B	H^A	H^B
(**12d**)	Me	Me	H	3.85	6.12	4.41	5.66
(**12e**)	Me	Et	H	3.65	6.09	4.19	5.56
(**34e**)[a]	Et	Me	H	3.84	6.01		
(**12f**)	Me	n-C_6H_{13}	H	3.72	6.07	4.28	5.56
(**34f**)[b]	n-C_6H_{13}	Me	H	3.85	6.08		
(**12i**)	Pr^n	Me	H	3.75	6.07	4.30	5.49
(**12n**)	Ph	Et	H	3.68	6.90	4.44	6.30

[a] From (**12e**) by a [1,3] phenylthio shift. [b] From (**12f**) by a [1,3] phenylthio shift.

calculated,[7] but those of the isomer assigned the *Z* configuration are further downfield by about the calculated amount than those of the *E* isomer. Table 2 gives a list of these values.

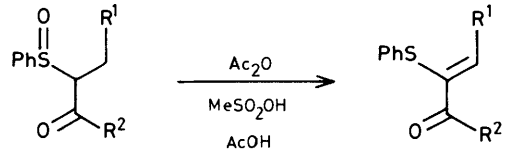
Another reason for assigning these configurations is the broadening of the higher field signal for the allylic proton A (Figure) in all compounds (**12**) due to homoallylic ($^5J_{AC}$ in **23**) coupling between the allylic proton A and the methyl group or CH_2 group in R^1 of the *Z*-isomer alone. This cannot be allylic coupling as the vinyl protons are not broadened and irradiation of the methyl doublet at δ 1.77 in (**12d**) (Figure) removed the broadening. Homoallylic coupling ($^5J_{HH}$) is normally larger when the protons are arranged *trans*, as in *Z*-(**12d**) or (**23**).[9]



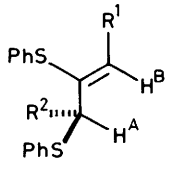
Z-(**23**) ($R^4CH_2 = R^1$)

Finally, the preferential formation of *E*-isomers in the rearrangement reaction and their isomerisation to *Z*-isomers under irradiation form a consistent picture.

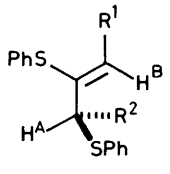
Stereochemistry and Mechanism.—The isomer ratios given in Table 2 were measured by n.m.r. spectrometry and give the composition of the allyl sulphide (**12**) as formed by rearrangement of adducts (**11**). This is not the thermodynamic ratio as in most cases the *Z*-isomer is more stable than the *E*. Thus the 50:50 mixture of (**12d**) isomerises with time to pure *Z*-(**12d**). This reaction is catalysed by light and occurs by the [1,3] phenylthio shift[4] which is degenerate for (**12d**). The thermodynamic preference for the *Z* configuration suggests that the 1,3 allylic interactions between R^1 and R^2, H_A, or phenylthio in *E*-(**24**) are worse than the 1,2 vinylic interactions between R^1 and phenylthio in *Z*-(**24**). This is clearly so from a study of models: for example both conformations (**24a**) and (**24b**) are worse for *E*-(**24**) than for *Z*-(**24**). A similar situation arises with the vinyl sulphides (**26**), formed by the Pummerer elimination from sulphoxides (**25**) as *E,Z* mixtures, but becoming almost pure *Z*-isomer with time, by reversible Michael addition of PhSH.



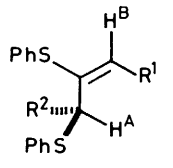
(**25**) *Z*-(**26**)



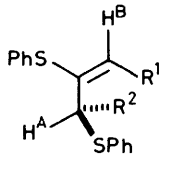
Z-(**24a**)



Z-(**24b**)



E-(**24a**)

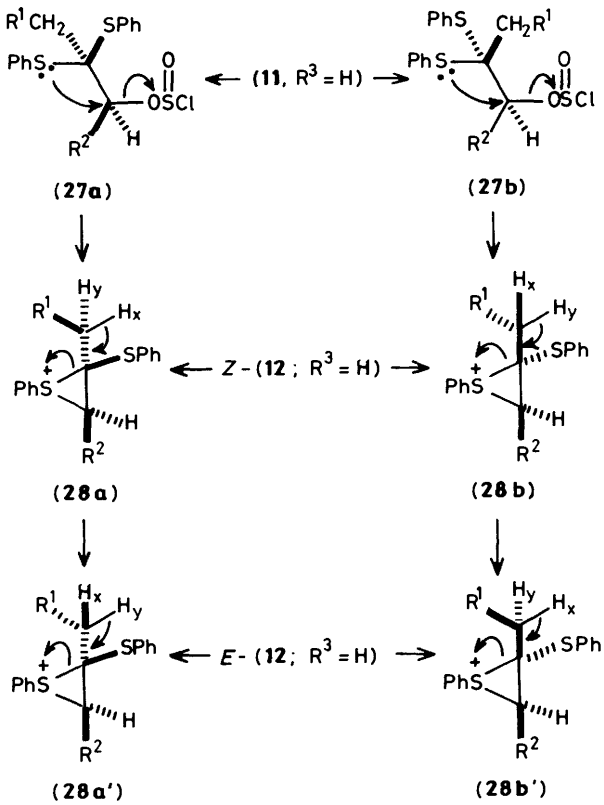


E-(**24b**)

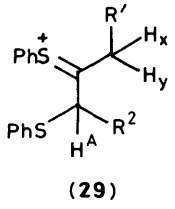
The formation of 50:50 mixtures of geometrical isomers or of mixtures rich in the less stable *E*-isomer of (**12**), suggests that loss of a proton occurs from the episulphonium ion (**28**) rather than from the rearranged cation (**29**), as the transition state for proton loss from the cation (**29**) would so closely resemble the products (**12**) that *Z*-(**12**) should be favoured. Either diastereotopic phenylthio group may migrate from (**27a**) or (**27b**) to give (**28a**) or (**28b**): either diastereotopic proton H_X or H_Y may be lost from (**28a**) or (**28b**) providing the C–H bond can get anti-peri-planar to the C–S^+ bond being broken as in the conformations shown so that (**28a**) and (**28b**) give *Z*-(**12**) but (**28a'**) and (**28b'**) give *E*-(**12**).

Whereas *Z*-(**12**) is favoured thermodynamically because PhSCHR is larger than phenylthio, there is little difference between (**28a**) and (**28b**) which are distinguished only by R^2 being *cis* to SPh or CH_2R^1 on the three-membered ring. The kinetic preference for *E* stereochemistry may arise because (**28a'**), (**28b**), and (**28b'**) are roughly equally stable, but (**28a**) is unstable because all substituents (R^1, SPh, and R^2) are on one surface of the molecule. If R^1 is large and rigid (Ph or RC=CH_2), (**27a**) is preferred to (**27b**) and (**28a'**) preferred to (**28a**) so that (**12l**—**n**) are formed as mostly *E* isomers.

In any case, if the loss of a proton occurred from (**29**), proton H_A is the best candidate as it is the most acidic and this would give ene disulphide (**13**) instead. The formation of (**13**) from (**11a**, **b**, **h**) may occur *via* (**29**). The episulphonium ion (**30**) is presumably also an intermediate in the rearrangement of (**16**)

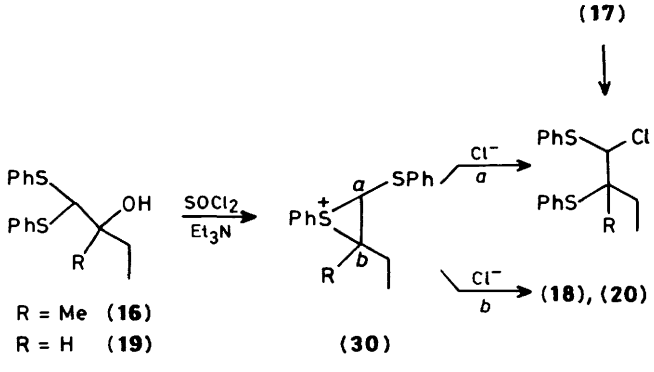


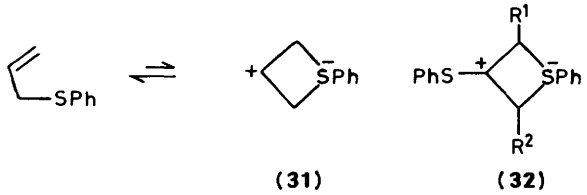
Scheme 2: Mechanism of the [1,2] phenylthio shift



(29)

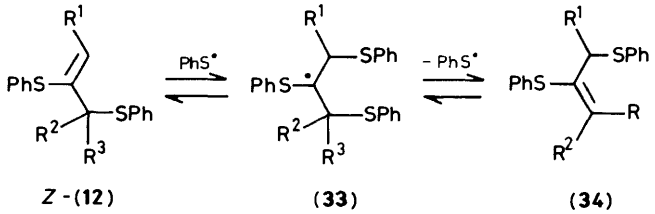
and (**19**): addition of chloride at *b* gives the unrearranged chlorides (**18**) and (**20**): addition at *a* gives the aldehyde (**17**) after hydrolysis.



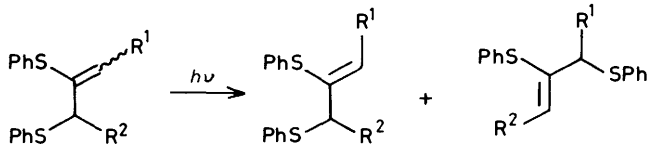


(31) (32)

The [1,3] *Phenylthio Shift.*—Kwart[10] has evidence that this reaction involves a dipolar intermediate (**31**) but we[2–4] and others[11] have evidence for a daylight- or phenylthio-initiated chain reaction which would involve intermediate (**33**) for the rearrangement of the bisphenylthio compounds (**12**). Either (**33**) or the Kwart intermediate (**32**) would be stabilised by the extra vinylic phenylthio group and the reaction is certainly more difficult to prevent than for the relatively stable sulphides (**6**) or (**22**). It occurs slowly in the dark, presumably initiated by the slow decomposition of (**12**) to PhSH, and rapidly on exposure to light (sunlight is best).

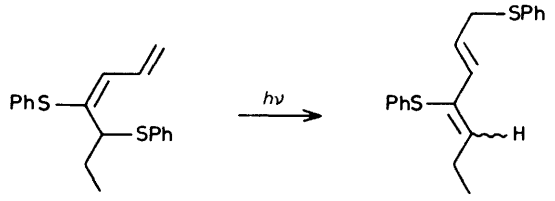


Z-(12) (33) (34)



(12; R3 = H) Z-(12; R3 = H) Z-(34; R3 = H)

The [1,3] phenylthio shift on symmetrical (**12d**) is degenerate and simply allows equilibrium of the *E*- and *Z*-isomers to give the more stable *Z* isomer. For aldehyde adducts (**12**; R^3 = H) with $R^1 \neq R^2$, the [1,3] phenylthio shift produces positional isomers (**12**) and (**34**). The simple alkyl derivatives (**12e**) and (**12f**) (Table 3) give a mixture of *Z*-(**12**) and *Z*-(**34**) in roughly equal proportions.* With a phenyl group to 'anchor' the double bond (**12n**), no (**34**) is produced but the pure *E*-(**12n**) formed from (**11n**) by rearrangement equilibrated to a 1:2 mixture of *Z* and *E*-(**12n**). The diene (**12l**) gave only the product of a [1,5]-phenylthio shift (**35**), resembling the [1,5] phenylthio shift observed for one α-phenylthio diene.[2]



E-(12l) (35)

The ketone adduct (**12q**) gave some product (**34**; R^1 = Et, R^2 = Me, R^3 = Ph) of a [1,3] phenylthio shift as a mixture of isomers but, without a phenyl group to attract the double bond, (**12p**) decomposed under irradiation with no sign of the tetrasubstituted olefin (**34**).

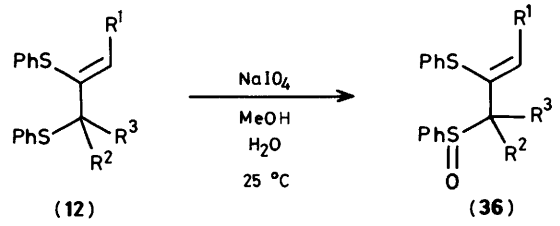
Use of the 2,3-*bisphenylthiopropenes* (**12**) *in Synthesis.*—The bisphenylthio compounds (**12**) have one allylic and one vinylic PhS group. The allylic sulphide may be oxidised with sodium metaperiodate in aqueous methanol at 25 °C to the sulphoxide (**36**) without affecting the vinyl sulphide, presumably

* See Table 2 for partial n.m.r. spectra of (**34e**) and (**34f**).

Table 3. Effect of light on bisphenylthiopropenes (**12**)

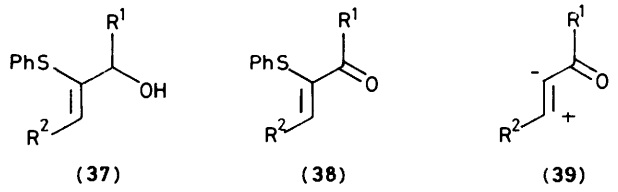
Compound[a]	Stereo E:Z	Products (yield, %) Z-(12)	Z-(34)	others
(12d)	1:1	100	*b*	
(12e)	3:2	50	50	
(12f)	3:2	67	33	
(12l)	*E*			*E*-(35), 60
				Z-(35), 40
(12n)	*E*	33		*E*-(12), 67
(12p)	2:1	*c*	*c*	*c*
(12g)	3:2	20	30	*E*-(34), 40

[a] See Table 1. [b] (**34d**) Is the same as (**12d**). [c] (**12p**) Decomposed on irradiation.



(**12**) (**36**)

because of the conjugation of the lone pair electrons on sulphur with the double bond. The conjugation with the phenyl group is also important as methyl vinyl sulphides are oxidised by the same reagent under even milder conditions (aqueous acetonitrile at 0 °C).[12] These sulphoxides (**36**) may be converted into 2-phenylthioallyl alcohols (**37**), 2-phenylthio enones (**38**), and 2-phenylthiobutadienes.[6,13]



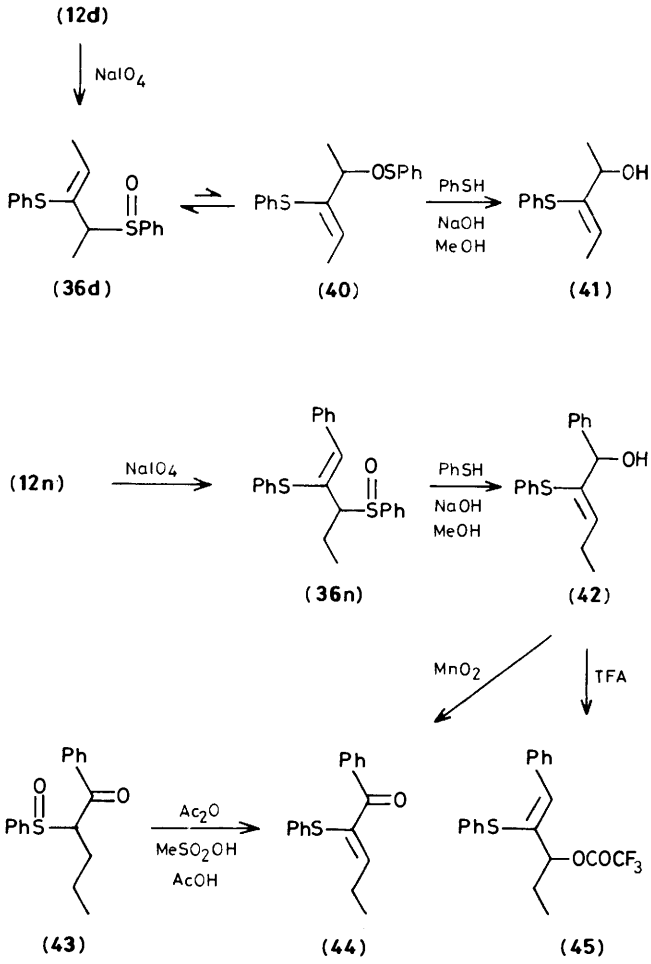
(**37**) (**38**) (**39**)

Cookson and Parsons[14] have reported the synthesis of 2-phenylthioallyl alcohols (**37**; R^2 = H) by the addition of phenylthiovinyl-lithium to carbonyl compounds and have used them to make 1,4-diketones. The enones (**38**) have been made by a number of routes,[15] mostly involving the Pummerer elimination, and have been used as Michael acceptors[15] and as Diels–Alder dienophiles.[16] Addition of a carbanion followed by alkylation and oxidative removal of sulphur allows the enones (**38**) to act as the synthons (**39**).

Our route to 2-phenylthioallyl alcohols (**37**) is by extension of the Evans–Mislow[17] rearrangement of the sulphoxides (**36**). Oxidation of either *Z*-(**12d**)* or a 1:1 mixture of *E* and *Z*-(**12d**) gave the same mixture of two sulphoxides (**36d**) in 89% yield. These gave a single 2-phenylthioallyl alcohol (**41**) on treatment with the thiophile PhSNa in methanol. The sulphoxide mixture also gave a single 2-phenylthiobutadiene (**48**) on thermolysis and is presumably a mixture of diastereoisomers (chiral S and C) of the *Z*-sulphoxide, equilibration between *E*- and *Z*-(**12d**) occurring during the oxidation.

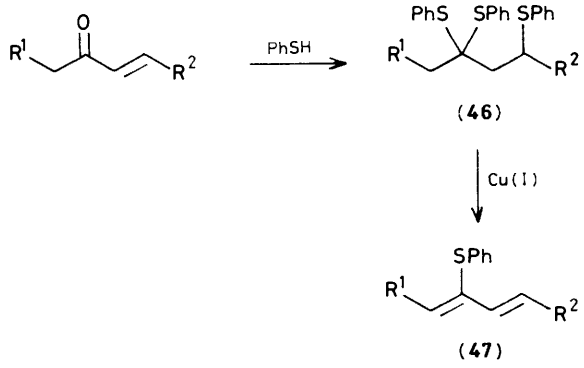
A [1,3] transposition[2,17,18] is involved in this synthesis of

* In our preliminary communication[6] we reported that (**12n**) was derived by a [1,3] phenylthio shift. While this shift would no doubt occur, (**12n**) was in fact made by rearrangement of (**11n**).



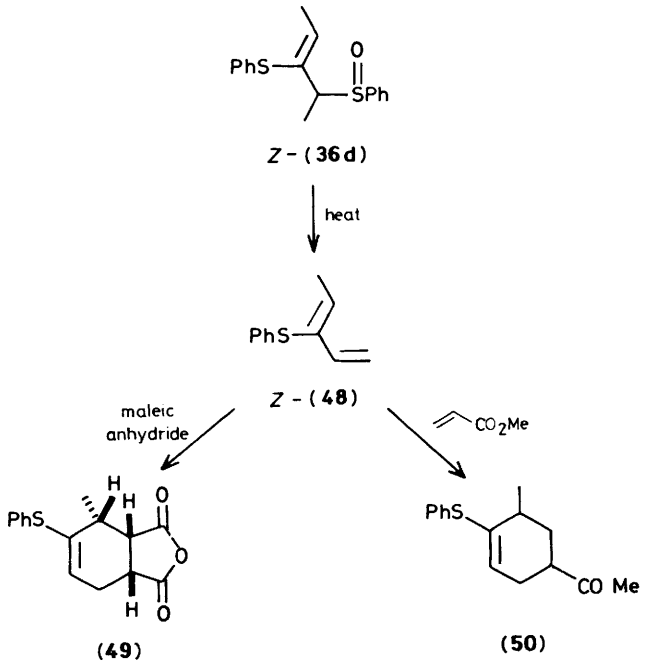
2-phenylthioallylic alcohols and it occurs even with (**36n**) when the product (**42**) has a less conjugated double bond than the starting material. Treatment of (**42**) with TFA gives the trifluoroacetate (**45**) of the more stable allylic alcohol, presumably *via* an allyl cation. The alcohol (**42**) is both benzylic and allylic and undergoes oxidation with manganese dioxide to give the α-phenylthio enone (**44**): the same compound can be made by Pummerer elimination on the α-phenylsulphinyl ketone (**43**).[19]

The 2-phenylthioallylic alcohols (**41**) and (**42**) and the 2-phenylthio enone (**44**) appear to be single geometrical isomers, presumably *Z*, by n.m.r. but the geometry is irrelevant for the applications described above.[14,15]

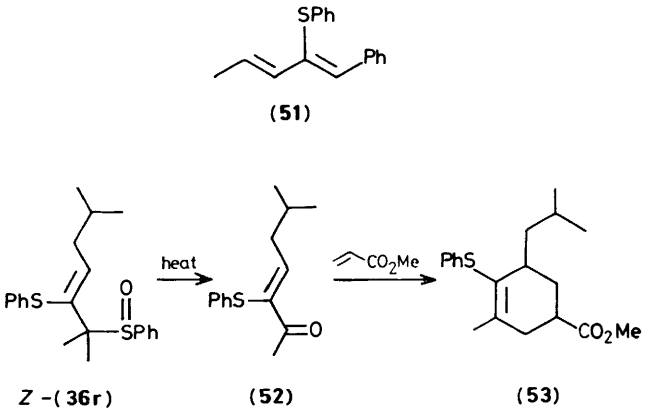


Phenylthiobutadienes are in demand for Diels–Alder reactions[20] as the phenylthio group is more powerful even than

RO in determining the regioselectivity of the reaction. 2-Phenylthiobutadienes give *'para'* adducts, *e.g.* (**50**) with unsymmetrical dienophiles, and the vinyl sulphide in these adducts is a masked ketone. Cohen[21] has made 2-phenylthiobutadienes (**47**) form enones by addition for three molecules of PhSH and Cu^{I}-catalysed elimination of two of them. It is not clear which product this elimination reaction would give if R^2 were an alkyl group and not hydrogen in (**46**).

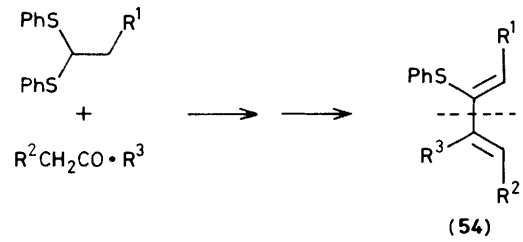


Thermolysis of sulphoxides (**36**) provides an alternative route to 2-phenylthiobutadienes. 'Symmetrical' (**36d**) gave 3-phenylthiopenta-1,3-diene (**48**) and hence adducts (**49**) and (**50**). The adduct (**49**) can be isolated in one step after heating sulphoxide (**48**) with maleic anhydride in benzene. Adduct (**49**) is a crystalline solid of sharp melting point whose n.m.r. spectrum appears to be that of a single diastereoisomer, while adduct (**50**) is an oil. The stereochemistry drawn for (**49**) is that of the *endo*-adduct of *Z*-(**36d**), but has not been rigorously proved.

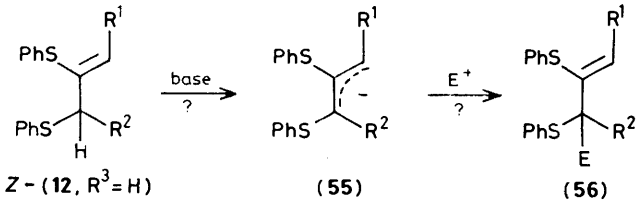


Thermolysis of sulphoxide (**36n**) gave a single geometrical isomer, presumably *E,Z*, of diene (**51**). Oxidation of a 1:1 mixture of *E* and *Z* (**12r**) gave a single sulphoxide (**36r**) (42%), some diene (**52**) (10%), and one isomer, presumably *E*, of unchanged (**12r**). Elimination of PhSOH from this tertiary alkyl sulphoxide is evidently very rapid and heating it briefly under reflux in benzene gave a good yield of the *Z*-diene (**52**) which added readily to methyl acrylate to give adduct (**53**) as an oil.

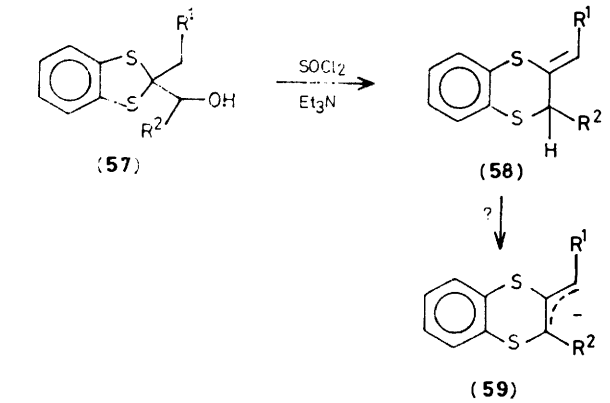
This synthesis of 2-phenylthiobutadienes is connective since the original bisphenylthio acetal and the carbonyl compound provide the two halves of the molecule (**54**). It also gives the best



geometrical isomer (*Z,E*) for Diels–Alder reactions. The main limitation is that only certain substitution patterns are useful, *i.e.* symmetrical ones like (**12d**), ones with the double bond anchored by a conjugating group like (**12n**), or cases like (**12r**) where only one geometrical isomer is oxidised. In other cases, it might be possible to use a mixture of dienes in the Diels–Alder reaction as the *Z,E*-isomer would react more rapidly.



Attempted Formation of Anions from the Bisphenylthio Compounds (**12**).—We had hoped[22] to use the anions (**55**) from the bisphenylthio compounds (**12**) as specific enol equivalents since the most likely products (**56**) would retain the vinyl sulphide as a masked ketone functionality. Treatment of (**12d**) with a base (Bu^nLi, Bu^sLi, LDA, KH, $KOBu^t$) in THF gave orange or red solutions typical of anions from allyl sulphides, but quenching the colour with electrophiles (D_2O, MeI, MeCHO, and PhCHO) gave either starting materials (**12d**) or mixtures of products, containing some adducts (by n.m.r.), from which no single compound could be isolated (Table 4).



One reason for this failure might be the difficulty of placing four substituents in the plane of the allyl anion (**55**). We hoped that the cyclic analogues (**58**), prepared[23] by rearrangement of the thioacetals (**57**) under the conditions used for the rearrangement of (**11**) to (**12**), might solve the problem as most

Table 4. Attempted preparation of anion and adducts from the bis-sulphide (**12d**)

Base	Complexing Agent	Temp. °C	Anion colour	Electrophile	Product
Bu^{n}Li		0	Red	D_2O	Mixture
		0	Red	MeCHO	Mixture
		0	Red	PhCHO	Mixture
	TMEDA	−78	Orange	D_2O	(**12d**)+?
	TMEDA	0	Red	D_2O	Mixture
	TMEDA	0	Red	PhCHO	Mixture
	HMPA	0	Red	MeI	Mixture
Bu^{s}Li	TMEDA	0	Red	MeI	(**12d**)+PhSMe
	HMPA	0	Red	MeI	(**12d**)+PhSMe
LDA		−78	Orange	PhCHO	Mainly (**12d**)
		−78	Orange	D_2O	(**12d**)
		−78 to −30	Red	D_2O	Mixture[a]
		0	Red	D_2O	Mixture[a]
	HMPA	−78	Red	PhCHO	S.M.
	HMPA	0	Red	MeI	*b,c*
	HMPA	0	Red	MeI	*c*
NaH		0	?	PhCHO	(**12d**)
KH		0	Red	PhCHO	(**12d**)
KH	HMPA	30	Yellow	MeI	(**12d**)
KOBu^t		0	Yellow	MeI	(**12d**)+*c*
Ph_3CLi		25	*d*	MeI	(**12d**)
MeMgI		38	No	MeI	(**12d**)

[a] 2 Equiv. of LDA used. [b] Excess of LDA used. [c] Mixtures of dialkylated products probably formed. [d] Any anion colour would be masked by the red Ph_3CLi.

of the eclipsing interactions in the anion (**59**) are already present in the alkylidene-1,4-benzodithian (**58**). However, no successful reactions of anions (**59**) with electrophiles were achieved.

Experimental

General spectroscopic and chromatographic details have been given elsewhere.[24] Details of experimental methods used with bisphenylthio acetals, such as 'Method C' were given in our earlier paper.[1]

1,1-*Bisphenylthiobut*-3-*ene* (**10**; R^1 = CH=CH_2).—n-Butyllithium (1.6M solution in hexane; 6.5 ml, 10.4 mmol) was added to bisphenylthiomethane (2.32 g, 10 mmol) in dry THF (40 ml) at 0 °C under nitrogen. After 15 min, allyl bromide (0.87 ml, 10.05 mmol) was added. The solution was stirred at room temperature for 1 h, poured into water (100 ml), and extracted with ether (3 × 25 ml). The combined extracts were washed with water (2 × 20 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give an oil. Distillation gave the *dithioacetal* (2.12 g, 78%) as a colourless oil, b.p. 172 °C/0.2 mmHg, $\nu_{max.}$(liq.) 1 635 (C=C), 1 578 cm^{-1} (PhS); δ($CDCl_3$) 7.6—7.0 (10 H, m, 2 SPh), 6.2—5.76 (1 H, m, CH_2CH=CH_2), 5.13 (1 H, d, J_{cis} 10 Hz, CH_2CH=C*H*), 5.10 (1 H, d, J_{trans} 16 Hz, CH_2CH=C*H*), 4.44 (1 H, t, *J* 6.5 Hz, PhSC*H*CH_2), and 2.62 (2 H, t, *J* 7 Hz, CHC*H*$_2$CH); *m/z* 272 (M^+, 8%), 163 (*M*-PhS, 100), 135 (PhSCH=CH_2, 36), and 109 (PhS, 65) (Found: C, 70.8; H, 6.15; S, 23.4. $C_{16}H_{16}S_2$ requires C, 70.5; H, 5.92; S, 23.5%).

3-*Methyl*-1,1-*bisphenylthiobut*-3-*ene* [**10**; R^1 = C(Me)=CH_2].—In a similar way, bisphenylthiomethane (2.32 g, 10 mmol), n-butyl-lithium (1.6M in hexane; 6.5 ml, 10.4 mmol), and methylallyl chloride (1.0 ml, 10.1 mmol) gave an oil. This was purified by column chromatography (80-fold excess of silica gel and using carbon tetrachloride as eluant) to give the *dithioacetal* (2.50 g, 87%) as a colourless oil, R_F (CCl_4) 0.37; $\nu_{max.}$(liq.) 1 642 (C=C) and 1 580 cm^{-1} (PhS); δ($CDCl_3$) 7.7—7.1 (10 H, m, 2 SPh), 4.88 and 4.82 (2 H, two s, C=C*H*$_2$), 4.53 (1 H, t, *J* 7 Hz, C*H*CH_2), 2.58 (2 H, d, *J* 7 Hz, CHC*H*$_2$), and 1.73 (3 H, s, Me); *m/z* 286 (M^+, 9%), 177 (*M* − SPh, 100), 135 (PhSC=CH_2, 30), 123 (PhSCH_2, 46), and 109 (PhS, 31) (Found: M^+, 286.0833. $C_{17}H_{18}S_2$ requires *M*, 286.0850).

2,2-*Bisphenylthiobutan*-1-*ol* (**11c**; R^1 = Me, R^2 = R^3 = H).—1,1-Bisphenylthiopropane[1] (390 mg, 1.5 mmol), TMEDA (0.3 ml, 2.1 mmol), n-butyl-lithium (1 ml of 1.7M in hexane), and paraformaldehyde (75 mg, added under a rapid stream of N_2) (Method C,[1] only one addition of n-butyllithium) gave the *dithioacetal* (307 mg, 71%) as a colourless oil, R_F (CH_2Cl_2) 0.35, $\nu_{max.}$(liq.) 3 450 br (OH) and 1 577 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.1 (10 H, m, 2 SPh), 3.50 (2 H, s, C*H*$_2$OH), 2.62 (1 H, s, OH, removed by D_2O), 1.68 (2 H, q, *J* 7 Hz, C*H*$_2$Me), and 1.11 (3 H, t, *J* 7 Hz, CH_2*Me*); *m/z* 181 (*M* − SPh, 74%), 151 (*M* − SPh − C_2H_6, 26), 110 (PhSH, 100), and 71 (*M* − SPh − PhSH, 47) (Found: C, 66.0; H, 6.45, S, 22.3. $C_{16}H_{18}OS_2$ requires C, 66.2; H, 6.24; S, 22.1%).

2-*Methyl*-3,3-*bisphenylthiohexan*-4-*ol* (**11j** = **14**; R^2 = Et).—2-Methyl-1,1-bisphenylthiopropane[1] (0.69 g, 2.5 mmol), TMEDA (0.39 ml, 2.7 mmol), n-butyl-lithium (1.6M in hexane; 1.6 ml, 2.56 mmol), and propionaldehyde (Method C) gave the *dithioacetal* (490 mg, 59%) as a colourless oil, R_F (CH_2Cl_2) 0.54, $\nu_{max.}$(liq.) 3 470 br (OH) and 1 578 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 SPh), 3.70 (1 H, dd, *J* 2.5 and 8 Hz, CH_2C*H*), 2.48 (1 H, s, OH, removed by D_2O), 2.34 (1 H, septuplet, *J* 6.5 Hz, C*H*Me_2), 1.95—1.4 (2 H, m, CHC*H*$_2$Me), 1.28 and 1.07 (6 H, two d, *J* 6.5 Hz, C*H*Me_2), and 0.90 (3 H, t, *J*, 7.5 Hz, CH_2*Me*) (Found: C, 68.6; H, 7.55; S, 19.0. $C_{19}H_{24}OS_2$ requires C, 68.6; H, 7.27; S, 19.3%).

1-*Phenyl*-2,2-*bisphenylthiopentan*-3-*ol* (**11n**; R^1 = Ph, R^2 = Et, R^3 = H).—2-Phenyl-1,1-bisphenylthioethane[1] (1.61 g, 5 mmol), TMEDA (0.78 ml, 5.4 mmol), n-butyl-lithium (1.6M in hexane; 3.5 ml, 5.6 mmol), and propionaldehyde (Method C) gave the *dithioacetal* (1.21 g, 64%) as a colourless oil, R_F (CH_2Cl_2) 0.60; $\nu_{max.}$(liq.) 3 480 br (OH) and 1 580 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.0 (15 H, m, 2 SPh and Ph), 3.54 (1 H, dd, *J* 2, 10 Hz, CH_2C*H*OH), 3.16 (2 H, ABq, *J* 14 Hz, CH_AH_BPh), 2.35 (1 H, s, OH, removed by D_2O), 2.2—1.3 (2 H, m, MeCH_2CHOH), and 0.90 (3 H, t, *J* 7 Hz, CH_2*Me*); *m/z* 321 (*M* − EtCHOH, 3%), 271 (*M* − SPh, 48), 161 (*M* − PhSH − PhS, 65), 110 (PhSH, 100), and 91 (PhCH_2, 92) (Found: *M* − EtCHOH, 321.0787. $C_{20}H_{17}S_2$ requires 321.0772; *M* − SPh, 271.1141. $C_{17}H_{19}OS$ requires 271.1157).

5-*Hydroxy*-4,4-*bisphenylthiohept*-1-*ene* (**11l**; R^1 = CH=CH_2, R^2 = Et, R^3 = H).—1,1-Bisphenylthiobut-3-ene (680 mg, 2.5 mmol), TMEDA (0.4 ml, 2.7 mmol), n-butyl-lithium (1.6M in hexane; 1.6 ml, 2.54 mmol) and propionaldehyde (Method C) gave an oil (840 mg). This was purified by column chromatography (100-fold excess of silica gel and using dichloromethane as eluant) to give the *dithioacetal* (432 mg, 52%) as a colourless oil, R_F (CH_2Cl_2) 0.44, $\nu_{max.}$(liq.) 3 470 br (OH), 1 632 (C=C), and 1 578 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 SPh), 6.01 (1 H, ddt, *J* 6.5, 10, 16 Hz, CH_2C*H*=CH_2), 5.2—4.8 (2 H, m, C=C*H*$_2$), 3.7—3.4 (1 H, m, CH_2C*H*OH) [this simplifies to 3.58 (1 H, dd, *J* 2.5, 9 Hz) with D_2O], 2.7—2.1 (2 H, m, C*H*$_2$CH=CH_2), 2.45 (1 H, d, *J* 6 Hz, CHO*H*), 2.1—1.4 (2 H, m, CHC*H*$_2$Me), and 0.97 (3 H, t, *J* 7.5 Hz, CH_2*Me*); *m/z* 330 (M^+ 0.1%), 271 (*M* − EtCHOH, 2), 221 (*M* − PhS, 39), and 110 (PhSH, 100) (Found: C, 68.8; H, 6.86; S, 19.0. $C_{19}H_{22}OS_2$ requires C, 69.0; H, 6.71; S, 19.4%).

5-*Hydroxy*-2-*methyl*-4,4-*bisphenylthiohept*-1-*ene* (**11m**; R^1 CMe=CH_2, R^2 = Et, R^3 = H).—3-Methyl-1,1-bisphenyl-

thiobut-3-ene (715 mg, 2.5 mmol), TMEDA (0.4 ml, 2.7 mmol), n-butyl-lithium (1.6M in hexane; 1.65 ml, 2.6 mmol), and propionaldehyde (Method C) gave an oil (1.2 g). This was purified by column chromatography (100-fold excess of silica gel and using dichloromethane as eluant) to give the *dithioacetal* (624 mg, 73%) as a colourless oil, R_F (CH_2Cl_2) 0.56, $\nu_{max.}$(liq.) 3 470 br (OH), 1 640 (C=C), and 1 580 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.1 (10 H, m, 2 SPh), 5.1 and 4.98 (2 H, two s, C=CH_2), 3.67 (1 H, ddd, *J* 2, 6, 10 Hz collapses to dd, *J* 2, 10 Hz with D_2O, CH_2CHOH), 2.57 (1 H, d, *J* 6 Hz, CHO*H* removed by D_2O), 2.71 and 2.39 (2 H, ABq, *J* 15 Hz, PhSCCH_AH_B), 2.2—1.4 (2 H, m, CHCH_2Me), 1.91 (3 H, s, CH_2=C*Me*), and 0.99 (3 H, t, *J* 7.5 Hz, CH_2*Me*); *m/z* 344 (M^+, 0.2%), 285 (*M* − EtCHOH, 5), 235 (*M* − SPh, 52), 225 (*M* − PhS − PhSH, 100), 110 (PhSH, 40), and 57 [$CH_2C(Me)$=CH_2, 32] (Found: M^+, 344.1282. $C_{20}H_{24}OS_2$ requires 344.1268).

4-*Hydroxy*-5,5-*bisphenylthiohept*-2-*ene* (**11g**; R^1 = Me, R^2 = MeCH=CH, R^3 = H).—1,1-Bisphenylthiopropane[1] (650 mg, 2.5 mmol), TMEDA (0.4 ml, 2.7 mmol), n-butyl-lithium (1.6M in hexane; 1.6 ml, 2.54 mmol), and crotonaldehyde (0.21 ml, 2.57 mmol) (Method C) gave the crude *dithioacetal* (quantitative yield) as an oil (purification was not attempted since in a previous experiment the dithioacetal decomposed on column chromatography), $\nu_{max.}$(liq.) 3 450 br (OH), 1 665 (C=C), and 1 580 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 SPh), 6.0—5.5 (2 H, m, CH=CH), 4.12 (1 H, d, *J* 5 Hz, CHC*H*OH), 2.65 (1 H, br s, OH, removed by D_2O), 2.0—1.2 (2 H, m, CH_2Me), 1.70 (3 H, d, *J* 4.5 Hz, C=CH*Me*), and 1.08 (3 H, t, *J* 7 Hz, CH_2*Me*); *m/z* 300 (*M* − C_2H_6, 3%), 259 (*M* − MeCH=CHCHOH, 15), 221 (*M* − PhS, 33), 151 (PhSCHEt, 33), and 110 (PhSH, 100) (Found: *M* − MeCH=CHCHOH, 259.0637. $C_{15}H_{15}S_2$ requires 259.0615; *M* − PhS, 221.1004. $C_{13}H_{17}OS$ requires 221.1001).

Synthesis of the Bis-sulphides (**12**)

3,4-*Bisphenylthiopent*-2-*ene* (**12d**; R^1 = R^2 = Me, R^3 = H).—Thionyl chloride (0.12 ml, 1.65 mmol) was added to an ice-cooled solution of the dithioacetal (**11d**) (293 mg, 0.97 mmol) in carbon tetrachloride (12 ml) and triethylamine (0.8 ml, 5.7 mmol) in a foil-wrapped flask. After 1 min the reaction mixture was poured into dilute hydrochloric acid (20 ml) and extracted with carbon tetrachloride (3 × 10 ml). The extract was washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give an oil, which was purified by preparative t.l.c. to give the *bis-sulphide* (250 mg, 90%) as a colourless oil, R_F (CH_2Cl_2) 0.77; $\nu_{max.}$(liq.) 1 628 (C=C) and 1 585 cm^{-1} (PhS); the n.m.r. spectrum showed a 1:1 mixture of geometrical isomers, δ($CDCl_3$) 7.6—6.9 (10 H, m, 2 SPh), 6.12(*Z*) and 5.66(*E*) (1 H, two q, *J* 7 Hz, C=C*H*Me), 4.41(*E*) and 3.85(*Z*) (1 H, two q, *J* 7 Hz, PhSC*H*Me), 1.75(*Z*) and 1.47(*E*) (3 H, two d, *J* 7 Hz, C=CHMe), and 1.45 (3 H, d, PhSCH*Me*); *m/z* 286 (M^+, 48%), 177 (*M* − SPh, 60), 149 (*M* − PhSCHMe, 100), and 110 (PhSH, 38) (Found: C, 71.0; H, 6.7; S, 22.7. $C_{17}H_{18}S_2$ requires C, 71.3; H, 6.33; S, 22.4%). When the product was left in sunlight for 1 or 2 days only the *Z* isomer remained. Isomerisation probably occurs *via* a [1,3] phenylthio shift.

3,4-*Bisphenylthiohex*-2-*ene* (**12e**; R^1 = Me, R^2 = Et, R^3 = H).—In a similar way, the dithioacetal (**11e**) (133 mg, 0.36 mmol) and thionyl chloride (0.06 ml, 0.8 mmol) gave the *bis-sulphide* (98 mg, 83%) as a colourless oil, R_F (CH_2Cl_2) 0.80; $\nu_{max.}$(liq.) 1 580 cm^{-1} (PhS); the n.m.r. spectrum showed a 40:60 mixture of geometrical isomers, δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 SPh), 6.09(*Z*) and 5.56(*E*) (1 H, two q, *J* 7 Hz, C=C*H*Me), 4.19(*E*) and 3.65(*Z*) (1 H, two t, *J* 7 Hz, C*H*CH_2), 2.2—1.65 (2 H, m, CHCH_2Me), 1.46 (3 H, d, *J* 7 Hz, C=CH*Me*), 0.97 and 0.95 (3 H, two t, *J* 7 Hz, CH_2*Me*); *m/z* 300 (M^+, 48%), 190 (*M* − PhSH, 100), and 110 (PhSH, 59) (Found: C, 72.2; H, 6.75; S, 21.5. $C_{18}H_{20}S_2$ requires C, 72.0; H, 6.71; S, 21.3%). When the product was left in sunlight for a few days, the n.m.r. spectrum showed a 1:1 mixture of *Z*-(**12e**) and one isomer (C) of (**34e**); δ($CDCl_3$) 7.6—7.0 (10 H, m, 2 SPh), 6.09(*Z*) and 6.01(C) [1 H, (q, *J* 7 Hz, C=C*H*Me) and (t, *J* 7 Hz, C=C*H*CH_2) respectively], 3.84(C) and 3.66(*Z*) (1 H, q, *J* 7 Hz, PhSC*H*Me and t, *J* 7 Hz, PhSC*H*CH_2), 2.21(C) and 2.01—1.60(*Z*) (2 H, quintet, *J* 7 Hz, CHCH_2Me and m, CHCH_2Me), 1.44(*Z*) and 1.1—0.74(*Z* + C) [6 H, d, *J* 7 Hz, C=CH*Me*(*Z*) and m, CH_2*Me*(*Z*), C=CH*Me*(C) and CH_2*Me*(C)].

3,4-*Bisphenylthiodec*-2-*ene* (**12f**; R^1 = Me, R^2 = n-C_6H_{13}, R^3 = H).—In a similar way the dithioacetal (**11f**) (125 mg, 0.33 mmol) and thionyl chloride (0.05 ml, 0.69 mmol) gave the *bis-sulphide* (115 mg, 96%) as a colourless oil, R_F (CH_2Cl_2) 0.82, $\nu_{max.}$ (liq.) 1 581 cm^{-1} (PhS); the n.m.r. spectrum showed a 40:60 mixture of *Z*(**12f**) and *E*-(**12f**); δ($CDCl_3$) 7.6—7.0 (10 H, m, 2 SPh), 6.07(*Z*) and 5.56(*E*) (1 Hz, two q, *J* 7 Hz, C=C*H*Me), 4.28(*E*) and 3.72(*Z*) (1 H, two t, *J* 7 Hz PhSC*H*CH_2), 2.0—1.6 (2 H, m, CHC*H*CH_2), 1.73(*Z*) and 1.42(*E*) (3 H, d, *J* 7 Hz, C=CH*Me*), 1.4—1.0 [8 H, m, $(CH_2)_4$Me], and 0.85 (3 H, distorted t, CH_2*Me*); *m/z* 356 (M^+, 46%), 247 (*M* − SPh, 100), and 109 (PhS, 46) (Found: M^+, 356.1635. $C_{22}H_{18}S_2$ requires 356.1631). When the product was left in sunlight for a few days the n.m.r. spectrum showed a 2:1 mixture of *Z*-(**12f**) and one isomer (C) of (**34f**); δ($CDCl_3$) 7.6—6.9 (10 H, m, 2 SPh), 6.08(*Z*) and 6.07(C) (1 H, q, *J* 7 Hz, C=C*H*Me and t, *J* 7 Hz, C=C*H*CH_2 respectively), 3.85(C) and 3.72(*Z*) (1 H, q, *J* 7 Hz, PhSC*H*Me and t, *J* 7 Hz, C=CHCH_2), 2.2—2.0(C) and 1.38—1.0(*Z* + C) [10 H, m, C=CHCH_2CH_2 and m, $(CH_2)_5$Me], 1.74(*Z*) and 1.44(C) (3 H, two d, C=CH*Me* and PhSCH*Me*), and 1.0—0.7 (3 H, m, CH_2*Me*).

1-*Phenylthio*-1-(1-*phenylthiocyclohexyl*)*prop*-1-*ene* [**12o**; R^1 = Me, R^2, R^3 = $(CH_2)_5$].—In a similar way the dithioacetal (**11o**) (108 mg, 0.3 mmol but rather impure) and thionyl chloride (0.04 ml, 0.55 mmol) gave the *bis-sulphide* (40 mg, 40%) as a colourless oil, R_F (CCl_4) 0.38, $\nu_{max.}$(liq.) 1 580 cm^{-1} (PhS); the n.m.r. spectrum showed a 2:3 mixture of *Z*-(**12o**) and *E*-(**12o**); δ($CDCl_3$) 7.6—7.0 (10 H, m, 2 SPh), 5.90(*Z*) and 5.62(*E*) (1 H, both q, *J* 8, 6.5 Hz, C=C*H*Me), 2.8—1.2 (10 H, m, cyclohexyl protons), 1.63(*E*) and 1.53(*Z*) (3 H, two d, *J* 6.5 and 7.5 Hz, C=CH*Me*) [the n.m.r. spectrum also showed 20% of the [1,3] PhS shifted component (**34o**): δ($CDCl_3$) 4.64 (1 H, q, *J* 7 Hz, PhSC*H*Me), and 1.43 (3 H, d, *J* 7 Hz, PhSCH*Me*)]; *m/z* 340 (M^+, 18%), 231 (*M* − PhS, 100), 121 (*M* − PhS − PhSH, 76), and 109 (PhS, 21) (Found: M^+, 340.1302. $C_{21}H_{24}S_2$ requires 340.1320).

2-*Phenylmethyl*-2,3-*bisphenylthiopent*-3-*ene* (**12p**; R^1 = R^2 = Me, R^3 = CH_2Ph).—In a similar way the dithioacetal (**11p**) (100 mg, 0.28 mmol) and thionyl chloride (0.05 ml, 0.69 mmol) gave the *bis-sulphide* (91 mg, 95%) as a colourless oil, R_F (CCl_4) 0.21, $\nu_{max.}$(liq.) 1 601 (C=C), and 1 581 cm^{-1} (PhS); the n.m.r. spectrum showed a 1:2 mixture of *Z*-(**12p**) and *E*-(**12p**); δ($CDCl_3$) 7.6—6.8 (15 H, m, Ph and 2 PhS), 5.95(*Z*) and 5.94(*E*) (1 H, two q, *J* 7.5 and 6.5 Hz, C=C*H*Me), 3.56 and 3.06 (*Z*) and 3.36 and 3.2 (*E*) (2 H, two ABq, *J* 14 Hz, CH_AH_BPh), 1.92(*Z*) and 1.65(*E*) (3 H, two d, *J* 7.5 and 6.5 Hz, C=CH*Me*), 1.50(*Z*) and 1.39(*E*) (3 H, two s, PhSC*Me*), *m/z* 376 (M^+, 13%), 285 (*M* − $PhCH_2$, 2), 263 (*M* − PhS, 34), 175 (*M* − $PhCH_2$ − PhSH, 27), 110 (PhSH, 39), and 91 ($PhCH_2$, 100) (Found: M^+, 376.1322. $C_{24}H_{24}S_2$ requires 376.1320). Exposure to sunlight for a few days decomposed the compound.

2-*Phenyl*-2,3-*bisphenylthiohex*-3-*ene* (**12q**; R^1 = Et, R^2 = Me, R^3 = Ph).—In a similar way the dithioacetal (**11q**) 207 mg, 0.53 mmol) and thionyl chloride (0.07 ml, 1 mmol) gave the *bis-*

sulphide (159 mg, 80%) as a colourless oil, R_F (CCl_4) 0.3, $\nu_{max.}$(liq.) 1 580 cm^{-1} (PhS); the n.m.r. spectrum showed a 40:60 mixture of *Z*-(**12q**) and *E*-(**12q**); δ($CDCl_3$) 7.7—6.7 (15 H, m, Ph and 2SPh), 6.54(*Z*) and 5.79(*E*) (1 H, two t, *J* 6.5 Hz, C=C*H*CH_2), 2.30(*Z*) and 1.64(*E*) (2 H, two quintets, *J* 7.5 Hz, CHCH_2Me), 1.84 and 1.83 (3 H, two s, PhC*Me*), and 0.96(*Z*) and 0.62(*E*) (3 H, two t, *J* 7 Hz, CH_2*Me*); *m/z* 268 (*M* + 1 − PhS, 13%), 266 (*M* − PhSH, 37), 157 (*M* − PhSH − PhS, 100). When exposed to sunlight for a few days it became mainly a 1:1 mixture of *E* and *Z*-(**13q**) [*ca.* 20% of *Z*-(**12q**) remained]; δ($CDCl_3$) 7.7—6.9 (15 H, m, Ph and 2 SPh), 4.36 and 3.98 (1 H, two t, *J* 7 Hz, PhSC*H*CH_2), 2.6—1.8 (2 H, m, CHCH_2Me), and 2.03 and 1.93 (3 H, both s, C=CMe), and 1.3—0.7 (3 H, m, CH_2*Me*).

2,3-*Bisphenylthiohept*-3-*ene* (**12i**; R^1 = n-Pr, R^2 = Me, R^3 = H).—In a similar way the dithioacetal (**11i**) (124 mg, 0.37 mmol) and thionyl chloride (0.06 ml, 0.84 mmol) gave the *bis-sulphide* (106 mg, 91%) as a colourless oil, R_F (CH_2Cl_2) 0.78, $\nu_{max.}$(liq.) 1 599 (C=C) and 1 580 cm^{-1} (PhS); the n.m.r. spectrum showed a 1:1 mixture of geometrical isomers, δ($CDCl_3$) 7.7—6.6 (10 H, m, 2 SPh), 6.07(*Z*) and 5.49(*E*) (1 H, two t, *J* 7 Hz, C=C*H*CH_2), 4.30(*E*) and 3.75(*Z*) (1 H, two q, *J* 7 Hz, PhSC*H*Me), 2.7—0.6 (7 H, m, CH_2CH_2*Me*), and 1.44 and 1.42 (3 H, two d, *J* 7 Hz, PhSCH*Me*); *m/z* 314 (M^+ 73%), 205 (*M* − PhS, 100), and 110 (PhSH, 80) (Found: C, 72.6; H, 7.1; S, 20.3. $C_{19}H_{22}S_2$ requires C, 72.6; H, 7.05; S, 20.4%). The effect of light on this compound was not investigated.

2,6-*Dimethyl*-2,3-*bisphenylthiohept*-3-*ene* (**12r**; R^1 = Bu^i, R^2 = R^3 = Me).—In a similar way the dithioacetal (**11r**) (478 mg, 1.33 mmol) and thionyl chloride (0.15 ml, 2 mmol) gave the *bis-sulphide* (347 mg, 76%) as a colourless oil, R_F (CCl_4) 0.30, $\nu_{max.}$(liq.) 1 580 cm^{-1} (PhS); the n.m.r. spectrum showed a 1:1 mixture of geometrical isomers, δ($CDCl_3$) 7.7—7.0 (10 H, m, 2 PhS), 6.02(*E*) and 5.88(*Z*) (1 H, two t, *J* 7 Hz, C=C*H*CH_2), 2.26(*E*) and 2.04(*Z*) (2 H, two t, *J* 7 Hz, CHCH_2CH), 2.0—1.2 (1 H, m, C*H*Me_2), 1.64(*E*) and 1.60(*Z*) (6 H, two s, PhSCMe_2), 0.88(*E*) and 0.73(*Z*) (6 H, both d, *J* 7 Hz, CHMe_2); *m/z* 342 (M^+, 17%), 233 (*M* − PhS, 91), 123 (*M* − PhS − PhSH, 58), and 110 (PhSH, 100) (Found: M^+, 342.1480. $C_{21}H_{26}S_2$ requires *M*, 342.1476). When exposed to sunlight for a few days the product became a 1:2 mixture of *Z*-(**12r**) and one isomer (C) of (**34r**), δ($CDCl_3$) 7.6—6.9 (10 H, m, 2 SPh), 5.88(*Z*) and 4.53(C) (1 H, t, *J*, 7 Hz, C=C*H*Me and t, *J* 7 Hz, PhSC*H*CH_2), 2.04(*Z*) and 2.0—1.2(*Z* + C) [3 H, t, *J* 7 Hz, C=CHCH_2 and m, CH_2CHMe_2(C) and C*H*Me_2(*Z*)], 1.86 and 1.65 (isomer C) and 1.60 [*Z*-(**12r**)] (6 H, two s, C=CMe_2 and s, PhSCMe_2), 0.92 and 0.85 (isomer C), and 0.73 [*Z*-(**12r**)] (6 H, all d, *J* 7 Hz, CHMe_2).

4,5-*Bisphenylthiohepta*-1,3-*diene* (**12l**; R^1 = CH=CH_2 R^2 = Et, R^3 = H).—In a similar way the dithioacetal (**11l**) (76 mg, 0.23 mmol) and thionyl chloride (0.04 ml, 0.55 mmol) gave the crude *bis-sulphide* (75 mg, 100%) as a colourless oil, $\nu_{max.}$(liq.) 1 621 (C=C) and 1 578 cm^{-1} (PhS); δ($CDCl_3$) 7.6—7.0 (10 H, m, 2 SPh), 6.8—6.0 (1 H, m, CHC*H*=CH_2), 5.79 (1 H, d, *J* 11 Hz, PhSC=C*H*CH), 4.89 (1 H, d, J_{cis} 10 Hz, CH=CH_2), 4.87 (1 H, d, J_{trans} 15 Hz, CH=CH_2), 4.32 (1 H, t, *J* 7.5 Hz, PhSC*H*Et), 2.2—1.7 (2 H, m, CHCH_2Me), and 1.04 (3 H, t, *J* 7 Hz); *m/z* 312 (M^+, 13), 203 (*M* − SPh, 100), 110 (PhSH, 72), 93 (*M* − PhSH − PhS, 97), and 77 (Ph, 78) (Found: M^+, 312.1003. $C_{19}H_{20}S_2$ requires *M*, 312.1006).

3,4-*Bisphenylthiohepta*-2,4-*diene* (**35**).—The crude bis-sulphide (**12l**) (75 mg) was subjected to preparative t.l.c. (CCl_4) to give an oil which after 1 h in the light at 30 °C gave the *bis-sulphide* (**35**) (52 mg, 72%) as a colourless oil, R_F (CCl_4) 0.28, $\nu_{max.}$(liq.) 1 581 cm^{-1} (PhS); the n.m.r. spectrum showed a 3:2 mixture of two geometrical isomers; δ($CDCl_3$) 7.6—7.0 (10 H, m, 2 SPh), 6.4—6.0 [3 H, m, C*H*=C*H*C(SPh)=C*H*], 3.6—3.4 (2 H, m, CHCH_2SPh), 2.42 and 2.21 (2 H, two quintets, *J* 7 Hz, CHCH_2Me), 1.0 and 0.98 (3 H, two t, *J* 7 Hz, CH_2*Me*); *m/z* 312 (M^+, 9%), 203 (*M* − PhS, 45), 123 (PhSCH_2, 25), 109 (PhS, 100), 93 (*M* − PhS − PhSH, 48), and 77 (Ph, 59) (Found: M^+ 312.1005. $C_{19}H_{20}S_2$ requires 312.1007).

2-*Methyl*-4,5-*bisphenylthiohepta*-1,3-*diene* [**12m**; R^1 = C(Me)=CH_2, R^2 = Et, R^3 = H].—In a similar way the dithioacetal (**11m**) (160 mg, 0.47 mmol) and thionyl chloride (0.06 ml, 0.82 mmol) gave, after work-up, an oil which was tentatively identified as a 2:1 mixture of geometrical isomers of the crude bis-sulphide (175 mg, >100%); δ($CDCl_3$) 7.7—7.0 (10 H, m, 2 SPh), 6.46 and 5.69 (1 H, two s, PhSC=C*H*), 5.1—4.4 (2 H, m, MeC=CH_2), 3.9—3.1 (1 H, m, PhSC*H*CH_2), 2.3—1.6 (2 H, m, CHCH_2Me), 1.43 and 1.26 (3 H, two s, *Me*C=CH_2), and 1.04 (3 H, t, *J* 7 Hz, CH_2*Me*). Preparative t.l.c. on the crude bis-sulphide gave a colourless oil (116 mg, 77%), R_F (CH_2Cl_2) 0.80, which n.m.r. showed to be mainly the product derived by a [1,5] phenylthio shift. However, the compound was still impure and was not fully characterised.

1-*Phenyl*-2,3-*bisphenylthiopent*-1-*ene* (**12n**; R^1 = Ph, R^2 = Et, R^3 = H).—In a similar way the dithioacetal (**11n**) (190 mg, 0.5 mmol) and thionyl chloride (0.06 ml, 0.8 mmol) gave the *bis-sulphide* (181 mg, 100%) as a colourless oil, R_F (CH_2Cl_2) 0.80, $\nu_{max.}$(liq.) 1 604 (C=C) and 1 580 cm^{-1} (PhS); the n.m.r. spectrum showed only *E*-(**12n**); δ($CDCl_3$) 7.7—6.7 (15 H, m, Ph and 2 SPh), 6.30 (1 H, s, C=C*H*Ph), 4.44 (1 H, t, *J* 7 Hz, C*H*CH_2), 2.3—1.7 (2 H, m, CHCH_2Me), and 1.03 (3 H, t, *J* 7 Hz, CH_2*Me*); *m/z* 362 (M^+, 33), 253 (*M* — SPh, 100), 143 (*M* − PhSH − PhS, 78), 109 (PhS, 14), and 77 (Ph, 8) (Found: M^+: 362.1174. $C_{23}H_{22}S_2$ requires 362.1163). When exposed to sunlight for a few days the product became a 1:2 mixture of *Z*-(**12n**) and *E*-(**12n**); δ($CDCl_3$) 7.7—6.7 (15 H, m, Ph and 2 SPh), 6.90(*Z*) and 6.30(*E*) (1 H, two s, C=CH), 4.44(*E*) and 3.68(*Z*) (1 H, two t, *J* 7 Hz, C*H*CH_2) 2.3—1.7(*Z* + *E*) (2 H, m, CHCH_2Me), and 1.03(*E*) and 1.00(*Z*) (3 H, two t, *J* 7 Hz, CH_2*Me*).

Reactions of Other Dithioacetals (**11**) *with* $SOCl_2$ *and* NEt_3.—(i) In a similar way the dithioacetal (**11h**; R^1 = Me, R^2 = Ph, R^3 = D) (133 mg, 0.36 mmol) and thionyl chloride (0.05 ml, 0.69 mmol) gave an oil (116 mg, 92%) which the n.m.r. spectrum showed to be a 2:1 mixture of (**12h**) and (**13h**); δ($CDCl_3$) 7.7—6.9 (15 H, m, Ph and 2 SPh), 6.64 and 5.64 (1 H, two q, *J* 7 Hz, C=C*H*Me in **12h**), 2.74 and 2.20 (2 H, two q, *J* 7 Hz, CH_2Me in **13h**), 1.89 and 1.66 (3 H, two d, *J* 7 Hz, C=CH*Me* in **12h**), 1.18 and 0.92 (3 H, two t, *J* 7 Hz, CH_2*Me*).

(ii) In a similar way the dithioacetal (**11a**; R^1 = R^3 = H, R^2 = Me) (1 mg, 0.31 mmol) and thionyl chloride (0.05 ml, 0.69 mmol) gave, after preparative t.l.c., a 2:1 mixture of *E* and *Z* isomers of the enedisulphide (**13a**) (70 mg, 82%) as a colourless oil, R_F (CH_2Cl_2) 0.8; δ($CDCl_3$) 7.6—7.1 (10 H, m, 2 SPh) and 2.18 and 1.97 (6 H, two s, 2 Me).

(iii) In a similar way the dithioacetal (**11b**; R^1 = R^3 = H, R^2 = Ph), (213 mg, 0.61 mmol) and thionyl chloride (0.1 ml, 1.4 mmol) gave, after preparative t.l.c., a 1:1 mixture of *E* and *Z* isomers of the enedisulphide (**13b**) (202 mg, 99%) as a colourless oil, R_F (CH_2Cl_2) 0.8; δ($CDCl_3$) 7.7—6.9 (15 H, m, Ph and 2 SPh) and 2.27 and 1.84 (3 H, two s, Me).

(iv) In a similar way the dithioacetals (**11j**) and (**11k**), (**11c**), and (**11g**) and thionyl chloride gave only complex mixtures of unidentified products.

(v) In a similar way the dithioacetal (**16**) (208 mg, 0.67 mmol) and thionyl chloride (0.08 ml, 1.1 mmol) gave an oil which on preparative t.l.c. gave the α-phenylthio aldehyde (**17**) (71 mg, 54%) as a colourless oil, R_F (CCl_4) 0.2, $\nu_{max.}$(liq.) 1 718 (C=O), and 1 580 cm^{-1} (PhS); δ($CDCl_3$) 9.30 (1 H, s, CHO), 7.6—7.0 (5

H, m, SPh), 1.71 (2 H, ABX_3, J^{AX} 7.5 Hz, CH_2Me), 1.24 (3 H, s, PhSC*Me*), and 1.0 (3 H, t, *J* 7.5 Hz, CH_2Me); *m/z* 194 (M^+, 17%), 165 (M − Et and/or M − CHO, 100), 123 ($PhSCH_2$, 39), and 110 (PhSH, 46) and the chloride (**18**) (80 mg, 36%) as a colourless oil, R_F (CH_2Cl_2) 0.4, $\nu_{max.}$(liq.) 1 580 cm^{-1} (PhS); δ($CDCl_3$) 7.7—7.0 (10 H, m, 2 SPh), 4.49 (1 H, s, PhSC*H*), 2.15—1.6 (2 H, m, CH_2Me), 1.44 (3 H, s, ClCMe), and 1.3—0.8 (3 H, m, CH_2Me); *m/z* 287 (M − Cl, 48), 178 (M − Cl − PhS, 100), and 110 (PhSH, 82).

(vi) In a similar way the dithioacetal (**19**) (220 mg, 0.76 mmol) and thionyl chloride (0.08 ml, 1.1 mmol) gave, after preparative t.l.c., the chloride (**20**) (62 mg, 26%) as a colourless oil, R_F (PhH) 0.80; δ($CDCl_3$) 7.6—6.9 (10 H, m, 2 SPh), 4.52 (1 H, d, *J* 3 Hz, PhSC*H*CH), 3.31 (1 H, dt, *J* 3, 3 and 10 Hz, CHC*H*CH_2), 2.6—2.0 and 1.9—1.4 (2 H, m, $CHCH_2Me$), and 1.11 (3 H, t, *J* 7.5 Hz, CH_2Me).

Preparation of the 2-Phenylthiobutadienes and their Diels–Alder Adducts.

2,6-*Dimethyl*-2-*phenylsulphinyl*-3-*phenylthiohept*-3-*ene* (**36r**).—Sodium metaperiodate (200 mg, 0.93 mmol) was added to a solution of the bis-sulphide (**12r**) (315 mg, 0.92 mmol) in methanol (20 ml) and water (3 ml) and the mixture stirred at room temperature in a foil-wrapped flask for 64 h. After partial evaporation, water (20 ml) was added and the mixture extracted with ether (3 × 20 ml). The extract was dried ($MgSO_4$) and evaporated under reduced pressure to give an oil which was purified by preparative t.l.c. to give the *sulphoxide* (137 mg, 42%) as a colourless oil, R_F (Et_2O) 0.68, $\nu_{max.}$(liq.) 1 615 (C=C), 1 580 (PhS), and 1 035 cm^{-1} (S=O); δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 SPh), 6.39 (1 H, t, *J* 7 Hz, C=C*H*CH_2), 2.4—1.9 (2 H, m, $CHCH_2CHMe_2$), 1.9—1.4 (1 H, m, C*H*Me_2), 1.54 and 1.33 (6 H, two s, PhSOCMe_2), and 0.89 (6 H, d, *J* 6.5 Hz, CHMe_2); *m/z* 342 (M − O, 0.1%), 249 (M − PhS, 3), 232 (M − PhSOH, 54), 110 (PhSH, 56), and 78 (PhH, 100) (Found: M − O, 342.1473. $C_{21}H_{26}S_2$ requires 342.1476; M + 1 − PhS, 250.1385. $C_{15}H_{22}OS$ requires 250.1391). Preparative t.l.c. also gave an oil (84 mg), R_F (Et_2O) 0.60, which was a mixture of *E*-(**12r**) and the diene (**52**) (see below).

2,6-*Dimethyl*-3-*phenylthiohepta*-1,3-*diene* (**52**).—A solution of the sulphoxide (**36r**) (113 mg) was heated under reflux in benzene (2 ml)) with a few crystals of hydroquinone for 1 h. The mixture was cooled, diluted with water (3 ml), and extracted with ether (3 × 5 ml); the extract was dried ($MgSO_4$) and evaporated under reduced pressure to give an oil. Preparative t.l.c. gave the *diene* (57 mg, 73%) as a colourless oil, R_F (CH_2Cl_2) 0.83, $\nu_{max.}$(liq.) 1 617 (C=C) and 1 580 cm^{-1} (PhS); δ($CDCl_3$) 7.14 (5 H, m, SPh), 6.34 (1 H, t, *J* 7 Hz, C=C*H*CH_2), 5.47 and 4.95 (2 H, two s, C=CH_2), 2.39 (2 H, t, *J* 7 Hz, $CHCH_2CHMe_2$), 1.96 (3 H, s, *Me*C=CH_2), 1.79 (1 H, nonet, *J* 6 Hz, CH_2CHMe_2), and 0.93 (6 H, d, *J* 6 Hz, CHMe_2); *m/z* 232 (M^+, 48%), 189 (M−$CHMe_2$, 61), 123 (M−PhS, 17), 110 (PhSH, 37), 79 (M−$CHMe_2$−PhSH, 100), and 77 (Ph, 61) (Found: M^+, 232.1298. $C_{15}H_{20}S$ requires 232.1286).

Methyl [3-*Methyl*-5-(2-*methylpropyl*)-4-*phenylthiocyclohex*-3-*ene*]-1-*carboxylate* (**53**).—A solution of the diene (**52**) (40 mg, 0.17 mmol) in methyl acrylate (0.15 ml, 1.6 mmol) was heated at 95—100 °C in a sealed tube with a trace of hydroquinone for 24 h. Evaporation gave an oil which was purified by preparative t.l.c. to give the *cyclohexene* (43 mg, 78%) as a colourless oil, R_F (CH_2Cl_2) 0.73, $\nu_{max.}$(liq.) 1 728 (C=O), 1 627vw (C=C), and 1 579 cm^{-1} (PhS); δ($CDCl_3$) 7.4—7.0 (5 H, m, SPh), 3.62 and 3.60 (3 H, two s, CO_2Me), 2.8—1.0 (9 H, m, $CH_2CHCH_2CHCH_2CHMe_2$), 1.94 (3 H, s, C=CMe), and 1.0—0.66 (6 H, m, CHMe_2); *m/z* 318 (M^+, 16%), 209 (M − PhS, 21), 149 [M − CO_2Me − PhSH, 58), 93 (C_6H_4Me) 67], and 58 ($CHMe_3$, 100) (Found: M^+, 318.1660. $C_{19}H_{26}O_2S$ requires *M*, 318.1653).

2-*Phenylsulphinyl*-3-*phenylthiopent*-3-*ene* (**36d**).—This was prepared in a similar way to the sulphoxide (**36r**) but using the bis-sulphide (**12d**) (254 mg, 0.88 mmol) and sodium metaperiodate (213 mg, 1 mmol) to give after 21 h the *sulphoxide* (236 mg, 89%) as a colourless oil, R_F (Et_2O) 0.5, $\nu_{max.}$(liq.) 1 619 (C=C), 1 580 (PhS), and 1 045 cm^{-1} (S=O); δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 Ph), 6.27 and 5.97 (1 H, two q, *J* 7 Hz, C=C*H*Me), 3.69 and 3.28 (1 H, two q, *J* 7 Hz, C*H*Me), 2.1—1.8 (3 H, m, C=CH*Me*), 1.25 and 1.23 (3 H, two d, *J* 7 Hz, PhSOCH*Me*); *m/z* 194 (M + 1 − PhS, 46%), 176 (M − PhSOH, 54), 149 (M − PhSOCHMe, 36), 126 (PhSOH, 45), and 110 (PhSH, 100) (Found: M + 1 − PhS, 194.0771. $C_{11}H_{14}OS$ requires 194.0765; M − PhSO·H, 176.0658. $C_{11}H_{12}S$ requires 176.0658; M − PhSO·CHMe, 149.0416. C_9H_9S requires 149.0424).

3-*Phenylthiopenta*-1,3-*diene* (**48**).—A solution of the sulphoxide (**36d**) (152 mg) in benzene (2 ml) was heated under reflux for 7 h. Work-up as before gave the *diene* (77 mg, 87%) as a colourless oil, R_F (CH_2Cl_2) 0.83, $\nu_{max.}$(liq.) 1 627 (C=C), and 1 584 cm^{-1} (PhS); δ($CDCl_3$) 7.3—6.9 (5 H, m, PhS), 6.40 (1 H, dd, *J* 10, 17 Hz, C*H*=CH_2), 6.33 (1 H, q, *J* 7 Hz, C=C*H*Me), 5.52 (1 H, d, J_{trans} 17 Hz, PhSCCH=C*H*), 5.00 (1 H, d, J_{cis} 10 Hz, PhSCCH=C*H*), and 1.96 (3 H, d, *J* 7 Hz, C=CH*Me*); *m/z* 176 (M^+, 49%), 110 (PhSH, 38), 67 (M − PhS, 91), and 41 (C_3H_5, 100) (Found: M^+, 176.0657. $C_{11}H_{12}S$ requires 176.0660).

3-*Methyl*-4-*phenylthiocyclohex*-4-*ene*-1,2-*dicarboxylic Anhydride* (**49**).—(a) The diene (**48**) (34 mg, 0.19 mmol) and maleic anhydride (20 mg, 0.2 mmol) were heated under reflux in benzene (1 ml) with a trace of hydroquinone for 10 h. Evaporation followed by trituration with light petroleum (b.p. 60—80 °C) gave the *cyclohexene* (27 mg, 51%) as a white solid. Recrystallisation from light petroleum gave white crystals, m.p. 120—121 °C, $\nu_{max.}$(liq.) 1 848 and 1 770 (C=O), 1 618vw, C=C), and 1 579 cm^{-1} (PhS); δ($CDCl_3$) 7.32 (5 H, s, PhS), 5.72 (1 H, t, *J* 5 Hz, C=C*H*CH_2), 3.5—3.1 (2 H, m, COC*H*C*H*CO), and 2.79 (1 H, quint., *J* 7 Hz, MeC*H*CH), 2.7—2.5 (2 H, m, C = $CHCH_2CH$), 1.24 (3 H, d, *J* 7.5 Hz, CH*Me*); *m/z* 274 (M^+, 100%), 246 (M − CO, 22), 231 (M − CO − Me, 16), 201 (M − 1 − OCOCO, 37), 110 (PhSH, 71), and 109 (PhS, 86) (Found: C, 64.6; H, 5.35; S, 11.6. $C_{15}H_{14}O_3S$. H_2O requires C, 64.6; H, 5.24; S, 11.5%).

(b) The sulphoxide (**36d**) (67 mg, 0.22 mmol) and maleic anhydride (23 mg, 0.23 mmol) were heated under reflux in benzene (1 ml) with a trace of hydroquinone for 9 h. The mixture was cooled, diluted with water (3 ml), and extracted with ether (3 × 5 ml) to give, after evaporation of the extracts, an oil. Crystallisation of this from light petroleum (b.p. 60—80 °C) gave the cyclohexene (**49**) (32 mg, 53%).

Methyl 3-*Methyl*-4-*phenylthiocyclohex*-4-*ene*-1-*carboxylate* (**50**).—A solution of the diene (**48**) (31 mg, 0.18 mmol) in methyl acrylate (0.15 ml, 1.6 mmol) was heated at 85—95 °C in a sealed tube with a trace of hydroquinone for 22 h. Evaporation of the mixture gave an oil which was purified by preparative t.l.c. to give the *cyclohexene* (32 mg, 69%) as a colourless oil, R_F (CH_2Cl_2) 0.52, $\nu_{max.}$(liq.) 1 725 (C=O) and 1 578 cm^{-1} (PhS); δ($CDCl_3$) 7.5—7.0 (5 H, m, PhS), 6.1—5.8 (1 H, m, C=C*H*CH_2), 3.7—3.6 (3 H, s, CO_2Me), 2.9—1.8 [6 H, m, $CHCH_2CH$-(CO_2Me)CH_2], and 1.3—0.9 (3 H, m, CH*Me*); *m/z* 262 (M^+, 52%), 203 (M − CO_2Me, 38), 153 (M − PhS, 28), 110 (PhSH, 16), 93 (M − PhSH − CO_2Me, 100), and 77 (Ph, 25) (Found: M^+, 262.1024. $C_{15}H_{18}O_2S$ requires *M*, 262.1028).

1-*Phenyl*-3-*phenylsulphinyl*-2-*phenylthiopent*-1-*ene* (**36n**).—This was prepared in a similar way to the sulphoxide (**36r**) but

using the bis-sulphide (**12n**) (220 mg, 0.61 mmol) and sodium metaperiodate (131 mg, 0.61 mmol) to give after 100 h. the *sulphoxide* (182 mg, 79%) as a colourless oil, R_F (Et_2O) 0.5, $\nu_{max.}$(liq.) 1 595 (PhS) and 1 035 cm^{-1} (S=O); δ($CDCl_3$) 7.8—6.9 (15 H, m, 2 SPh and Ph), 6.89 and 6.58 (1 H, two s, C=C*H*), 3.17 and 3.39 (1 H, two dd, *J* 6, 8 Hz, PhSO·C*H*CH_2), 2.2—1.7 (2 H, m, CH_2Me), and 0.90 and 0.83 (3 H, two t, *J* 7.5 Hz, CH_2*Me*); *m/z* 378 (*M*$^+$, 0.6%), 362 (*M* − O, 1), 270 (*M* + 1 − PhS), 252 (*M* − PhSOH, 66), 211 (*M* − PhSOCHEt, 9), 167 (PhSOCHEt, 20), 143 (*M* − PhS − PhSOH, 100), 110 (PhSH, 93), and 77 (Ph, 41) (Found: *M*$^+$, 378.1115. $C_{23}H_{22}OS_2$ requires *M*, 378.1112).

1-*Phenyl*-2-*phenylthiopenta*-1,3-*diene* (**51**).—A solution of sulphoxide (**36n**) (184 mg) in benzene (2 ml) was heated under reflux with a few crystals of hydroquinone for 6 h. Work-up as before gave the *diene* (76 mg, 62%) as a colourless oil, R_F (CCl_4) 0.43, $\nu_{max.}$(liq.) 1 635 (C=C) and 1 578 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 SPh), 7.0—6.1 (3 H, m, vinyl H), and 1.74 (3 H, d, *J* 4 Hz, CH*Me*); *m/z* 252 (*M*$^+$, 49%), 1.43 (*M* − PhS, 56), 128 (*M* − PhSMe, 100), 109 (PhS, 55), and 91 ($PhCH_2$, 39) (Found: *M*$^+$, 252.0971. $C_{17}H_{16}S$ requires *M*, 252.0972).

4-*Hydroxy*-3-*phenylthiopent*-2-*ene* (**41**).—Sodium thiophenoxide, prepared by dissolving sodium hydroxide (163 mg, 4 mmol) in thiophenol (340 mg, 3.1 mmol) and methanol (10 ml), was added to the sulphoxide (**36d**) (97 mg, 0.32 mmol) and the solution stirred at room temperature. After 30 min, the mixture was poured into 10% aqueous sodium hydroxide (20 ml) and extracted with ether (3 × 10 ml). The combined extracts were washed with water (2 × 5 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give an oil, which was purified by preparative t.l.c. to give the *allyl alcohol* (50 mg, 81%) as a colourless oil, R_F (CH_2Cl_2) 0.15; $\nu_{max.}$(liq.) 3 360 br (OH) and 1 670 cm^{-1} (C=C); δ($CDCl_3$) 7.22 (5 H, s, Ph), 6.41 (1 H, q, *J* 7 Hz, C=C*H*Me), 4.32 (1 H, q, *J* 6.5 Hz, C*H*Me), 2.15 (1 H, s, OH, removed by D_2O), 1.87 (3 H, d, *J* 7 Hz, C=CH*Me*), and 1.33 (3 H, d, *J* 6.5 Hz, CH*Me*), *m/z* 194 (*M*$^+$, 100%), 149 (*M* − MeCHOH, 41), 110 (PhSH, 47), and 85 (*M* − SPh, 26) (Found: C, 68.2; H, 7.52; S, 16.2. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.26; S, 16.5%).

1-*Hydroxy*-1-*phenyl*-2-*phenylthiopent*-2-*ene* (**42**).—This compound was prepared in a similar way to the allyl alcohol (**41**) but using the sulphoxide (**36n**) (178 mg, 0.47 mmol) and sodium thiophenoxide (320 mg, 2.4 mmol) to give the *allyl alcohol* (95 mg, 75%) as a colourless oil, R_F (CH_2Cl_2) 0.4; $\nu_{max.}$(liq.) 3 380 br (OH), 1 625w (C=C), and 1 580 cm^{-1} (PhS); δ($CDCl_3$) 7.3—6.9 (10 H, m, SPh and Ph), 6.24 (1 H, t, *J* 7 Hz, C=C*H*CH_2), 4.98 (1 H, s, PhC*H*OH), 2.55 (1 H, s, OH, removed by D_2O), 2.28 (2 H, quint., *J* 7.5 Hz, CHCH_2Me), and 0.96 (3 H, t, *J* 7.5 Hz, CH_2*Me*); *m/z* 270 (*M*$^+$, 52%), 164 (PhSCH=CHEt, 18), 85 (MeCH_2CH=CCH_2OH, 65), 83 (CH_2=CH–CH=C–CH_2OH, 100), and 77 (Ph, 30) (Found: *M*$^+$, 270.1078. $C_{17}H_{18}OS$ requires *M*, 270.1078).

1-*Phenyl*-2-*phenylthiopent*-1-*en*-3-*yl Trifluoroacetate* (**45**).—The allyl alcohol (**42**) (67 mg) was dissolved in chloroform (3 ml) and TFA (0.3 ml) was added. The solution was stirred at room temperature for 5 min, poured into saturated aqueous sodium carbonate (10 ml), and extracted with chloroform (3 × 5 ml). The extract was washed with water (2 × 5 ml), dried ($MgSO_4$), and evaporated to give an oil which was purified by preparative t.l.c. to give the *trifluoroacetate* (69 mg, 76%) as a colourless oil, R_F (CH_2Cl_2) 0.7, $\nu_{max.}$(liq.) 1 780 (C=O) and 1 580 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.0 (11 H, m, Ph, SPh, and PhC*H*=C), 5.42 (1 H, t, *J* 6 Hz, C*H*CH_2), 2.00 (2 H, quint., *J* 7 Hz, CHCH_1Me), and 0.94 (3 H, t, *J* 7 Hz, CH_2*Me*); *m/z* 366 (*M*$^+$, 10), 252 (*M* − CF_3CO_2H, 14), 211 (*M* − EtCHCO_2CF_3, 17), 143 (*M* − CF_3CO_2H − SPh, 47), 128 (*M* − CF_3COOH − SPh − Me, 41), and 110 (PhSH, 43) (Found: *M*$^+$, 366.0898, $C_{19}H_{17}F_3O_2S$ requires 366.0901).

1-*Phenyl*-2-*phenylthiopent*-2-*en*-1-*one* (**44**).—Activated manganese dioxide[25] (275 mg, 3.16 mmol) was added to a solution of the allyl alcohol (**42**) (60 mg, 0.22 mmol) in dry ether (2 ml). The mixture was stirred at room temperature for 18 h, after which additional MnO_2 (140 mg) was added and stirring was continued for a further 26 h. Filtration through Celite followed by further ether washings (5 × 5 ml) gave, on evaporation of the filtrate, the *enone* (33 mg, 55%, 65% on recovered starting material) as a colourless oil, R_F (CH_2Cl_2) 0.54, $\nu_{max.}$(liq.) 1 656 (CO), 1 592 (CO), and 1 576 cm^{-1} (PhS); δ($CDCl_3$) 7.8—7.0 (10 H, m, PhS and Ph), 6.70 (1 H, t, *J* 7 Hz, C=C*H*CH_2), 2.58 (2 H, quint., *J* 7 Hz, CHCH_2Me), and 1.12 (3 H, t, *J* 7 Hz, CH_2*Me*); *m/z* 268 (*M*$^+$, 40%), 163 (*M* − COPh, 12), 159 (*M* − PhS, 30), 109 (PhS, 23), 105 (PhCO, 100), and 77 (Ph, 100) (Found: *M*$^+$, 268.0909. $C_{17}H_{16}OS$ requires *M*, 268.0922).

Acknowledgements

We thank the S.E.R.C. for a grant (to P. B.).

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Received 31*st August* 1984; *Paper* 4/1509