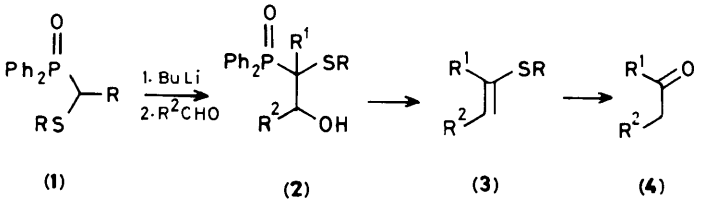
Phenylthioallyl and Phenylthiovinyl Phosphine Oxides: Synthesis of 1-Phenylthiobutadienes and a Three-component Synthesis of Ketones

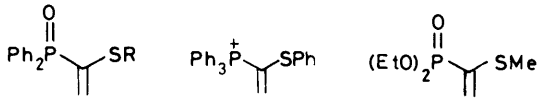
J. Ian Grayson, Stuart Warren,* and Alex T. Zaslona
University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

The functionalisation of some substituted allyl and vinyl diphenylphosphine oxides is explored and routes to substituted γ-phenylthioallyl and γ-phenylthiovinyl phosphine oxides are described. These reagents are used in the synthesis of the title compounds.

We have described the use of α-phenylthioalkyl- and α-methylthioalkyl-diphenylphosphine oxides (**1**) in the Horner-Wittig reaction [1] for the synthesis of ketones (**4**) *via* the vinyl sulphides (**3**) and the rearrangement [2] of the intermediate alcohols (**2**) with diphenylphosphinoyl (Ph_2PO), phenylthio (PhS), or methylthio (MeS) migration. We now describe a three-component synthesis [3] of the same intermediates (**2**) *via* 1-phenylthiovinyldiphenylphosphine oxide (**5**; R = Ph) and the extension of these reactions to sulphenylated allylic diphenylphosphine oxides.



(**1**) (**2**) (**3**) (**4**)

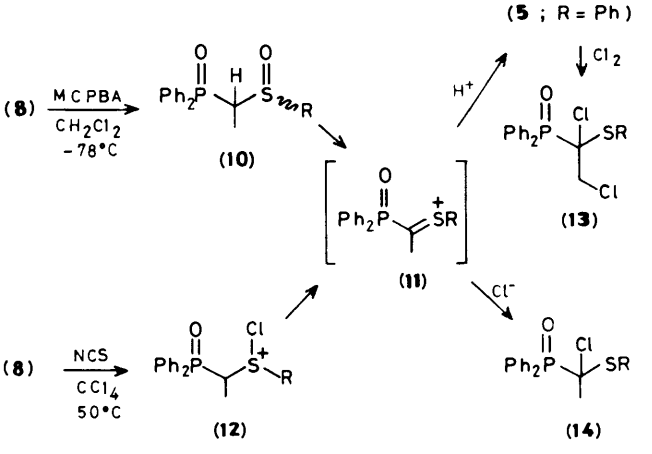


(**5**) (**6**) (**7**)

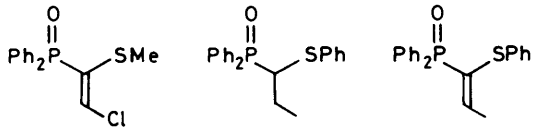
The phosphonium salt [5] (**6**) and the phosphonate ester [6] (**7**) capture nucleophiles to give carbanions which react with aldehydes and ketones to give vinyl sulphides and hence longer chain ketones by alkylative carbonyl transposition.[7] The corresponding phosphine oxides (**5**; R = Me, Ph) can be made from the saturated compounds (**8**; R = Me, Ph). Direct sulphenylation of ethyldiphenylphosphine oxide gives a 1:1:1 mixture of starting material, product (**8**; R = Ph), and (**9**). An Arbuzow reaction between Ph_2POEt and 1-chloroethyl phenyl sulphide gives 25% of (**8**; R = Ph) after chromatography. Methylation of the anions of (1; R^1 = H, R^2 = Me, Ph) is the best route to (**8**), while direct sulphenylation of the alkyl diphenylphosphine oxides is the best route to compounds with longer alkyl chains.[1]

(**8**) (**9**)

The ability of sulphur to transfer functionality to an adjacent carbon atom [8] is the basis for the next step. Oxidation of (**8**; R = Ph) gave a 1:1 mixture of sulphoxides (**10**), which could be separated by h.p.l.c. The Pummerer elimination procedure,[9] in which the sulphoxides are acetylated (Ac_2O) under acidic conditions, gave a good yield of (**5**; R = Ph) but required 8 days at room temperature. Attempts to speed up the reaction by heating caused decomposition. Direct chlorination of the sulphide (**8**; R = Ph) gave the α-chloro sulphide (**14**; R = Ph), *via* (**12**; R = Ph) and the Pummerer intermediate (**11**; R = Ph). A by-product from this reaction was the dichloro compound (**13**; R = Ph), presumably formed by chlorination of (**5**; R = Ph). Separation of this mixture by chromatography on silica, gave (**5**; R = Ph, 66%), the elimination of HCl evidently occurring on the silica. Treatment of the mixture with $ZnBr_2$ similarly gave (**5**; R = Ph, 62%) and (**13**; R = Ph).

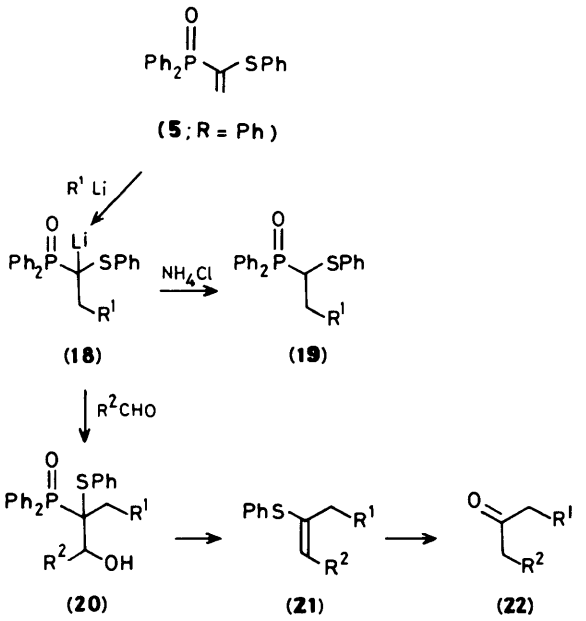


The methylthio analogue (**5**; R = Me) prepared directly from the saturated compound (**8**; R = Me) by chlorination as (**14**; R = Me) is unstable under the reaction conditions. The dichloro compound (**13**; R = Me) is also unstable and gives (**15**) with $ZnBr_2$. The homologue (**17**) was made as a 1:1 *E*:*Z* mixture by chlorination of (**16**) (65%) or by the Pummerer elimination procedure on the corresponding sulphoxide (76%). Attempts to make (**5**; R = Ph) from (1; R = Ph, R^1 = H) by Mannich-style reactions or by alkylation with $PhSCH_2Cl$ failed.



Z-(15) (16) Z-(17)

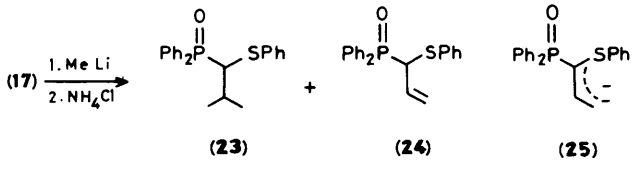
Addition of alkyl-lithiums to the Michael acceptor (5; R = Ph) occurred cleanly with MeLi, BuLi, and Bu^{s}Li but in lower yield with PhLi. In each case the lithium derivative (18) could be trapped with ammonium chloride to give the α-phenylthioalkyldiphenyl phosphine oxides (19). The methylthio analogue (5; R = Me) gave no adduct with MeLi or BuLi.



(5; R = Ph)

(18) (19) (20) (21) (22)

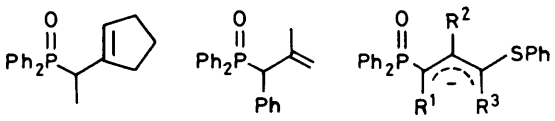
Trapping the lithium derivatives (18) with aldehydes gave moderate yields of the vinyl sulphides (21), presumably *via* the adducts (20), and these could be hydrolysed to the ketones (22) with trifluoroacetic acid (TFA).[1] Addition of (18) to ketones, as expected,[1] gave none of the corresponding adducts. The publication of Hewson's[5] and Mikolajczak's[6] much fuller studies of the better reagents (6) and (7) brought this work to a halt.



(23) (24) (25)

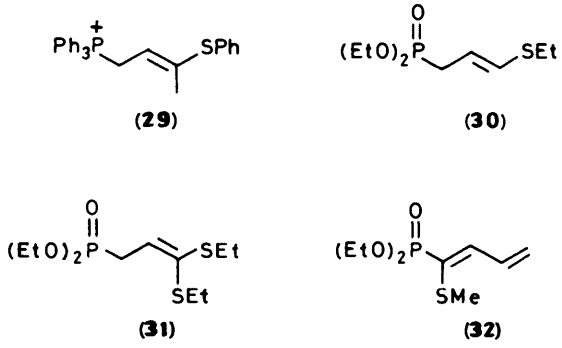
The homologue (17) does add MeLi but only 42% of the adduct (23) was isolated. The remainder (44% isolated) was a mixture of starting material and the sulphenylated phosphine oxide (24), presumably from deprotonation of (17) to give the allyl anion (25), reprotonation of which gives (17) or (24). We attempted the addition of Me_2CuLi and the anion of dimethyl malonate, but no reaction occurred in either case. The remainder of this paper concerns the chemistry of anions such as (25).

Sulphenylated Allylic Phosphine Oxides.—In general, anions of allylic phosphine oxides react in the α-position with electrophiles.[10,11] Exceptions include reactions of the anion of the cyclopentenyl compound[11] (26) with CO_2, PhCHO, and PhSSPh, and of the anion of the α-phenyl compound (27) with PhCHO. Anions of allyl sulphides generally react α with alkylating agents but γ with carbonyl compounds.[12] We have therefore studied the reactions of allyldiphenylphosphine oxide and its anion with electrophiles, particularly sulphenylating agents, since anions of allylic phosphine oxides (28) with a γ-PhS groups should react regiospecifically α to Ph_2PO (*i.e.* γ to PhS) with carbonyl compounds.



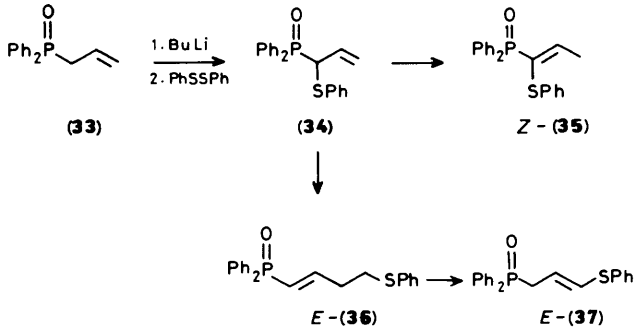
(26) (27) (28)

Phosphonium salts (29) have been made[13] by addition of Ph_3PH^+ to 2-phenylthiobutadienes, and esters with one[14] (30) or two[15] (31) γ-EtS groups by direct displacement of halide by EtS^-. The esters (31) have been used[15] in Wittig reactions. Anions of α-methylthioallyl phosphonate esters have been formed[16] by addition of nucleophiles to the diene (32) and also used in Wittig reactions.



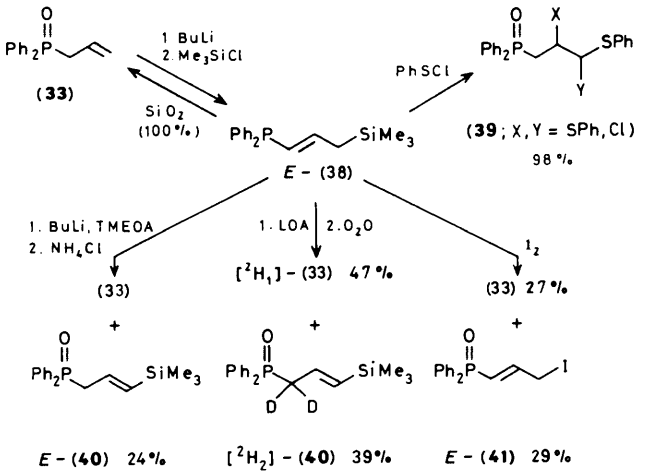
(29) (30) (31) (32)

Sulphenylation of the anion of allyldiphenylphosphine oxide (33) with PhSSPh under various conditions gave mixtures of the α-adduct (35), one geometrical isomer of the γ-adduct (36), and both geometrical isomers of the γ-adduct (37). All these products can arise from the α-adduct (34): (35) by a double bond shift, (36) by a [1,3]PhS shift,[17] and (37) by both. The mixture could not be separated by chromatography.



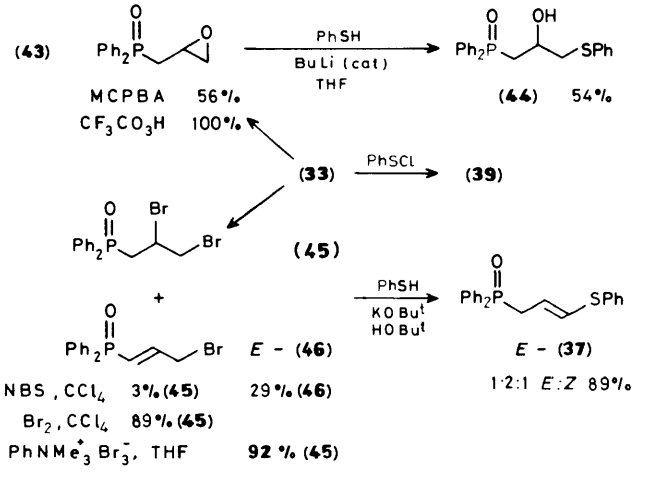
(33) (34) Z-(35) E-(36) E-(37)

Silylation of the anion of (33) (BuLi, Me_3SiCl) gave an excellent yield of the γ-product (38), but attempted sulphenylation of this in the presence of Lewis acids (SiO_2, BF_3, or $ZnBr_2$) or fluoride ion gave no (37). Other reactions of (38) are summarised in Scheme 1. Desilylation occurs very easily so that mixtures of products with and without the $SiMe_3$ group are formed. Sulphenylation without Lewis acid (PhSCl at 0 °C) gave only the products of desilylation, a mixture of regioisomers (39).



Scheme 1.

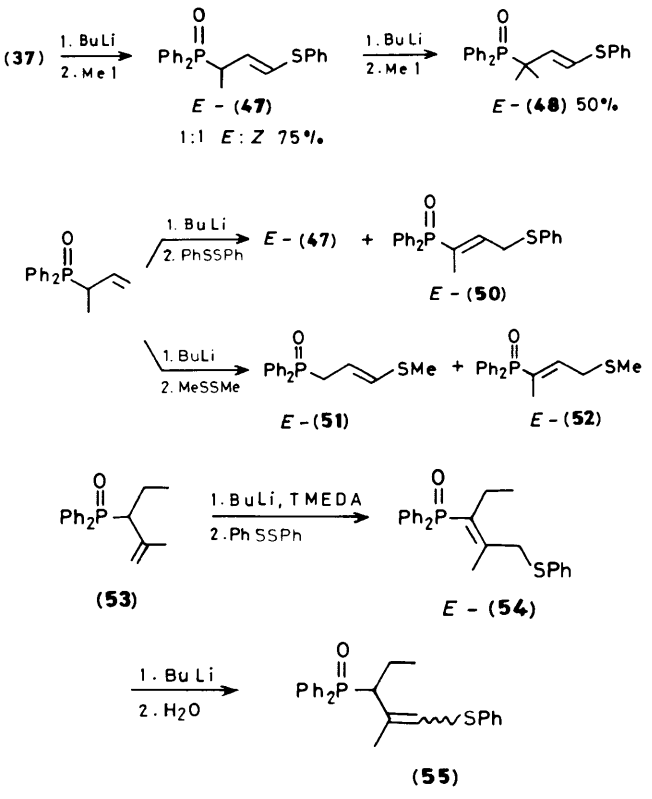
Chlorination of allyl phenyl sulphide with *N*-chlorosuccinimide (NCS) and displacement of chloride from (**42**) with Ph_2P^- followed by oxidation (H_2O_2) gave some (**37**) but the best synthesis came from a study of electrophilic attack on (**33**), summarised in Scheme 2. The epoxide (**43**) could be prepared in excellent yield but addition[18] of PhS^- to it gave only a moderate yield of the alcohol (**44**). Finally, bromination under the right conditions gave an excellent yield of the dibromide (**45**) which gave the γ-phenylthioallylphosphine oxide (**37**) on treatment with PhSH in base. We have used the same intermediate (**45**) in the synthesis of a γ-aminoallylphosphine oxide.[19]



Scheme 2.

Substituted γ-phenylthioallylic phosphine oxides are more straightforward to make. Alkylation of (**36**) or (**37**) (BuLi, MeI) occurred exclusively in the position α to Ph_2PO (and therefore γ to PhS) to give (**47**) in 75% yield. A second methylation occurred at the same site to give (**48**). Evidently the Ph_2PO group, like the CO_2R group,[20] dominates allyl anion reactivity when in competition with the PhS group, at least towards alkylation. Alternatively, sulphenylation (PhSSPh) of the anion (BuLi) of the allylphosphine oxide[21] (**49**) gave a mixture of the γ-adducts *E*-(**47**) and *E*-(**50**). Similarly MeSSMe gave a mixture of *E*-(**51**) and *E*-(**52**). These mixtures were not separated as the same allyl anion should be formed from either component.

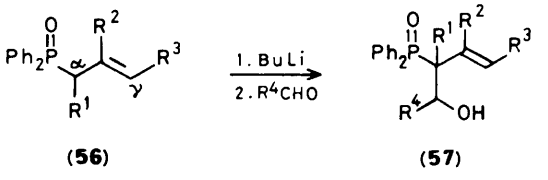
More highly substituted compounds can be made in the same way. We have already reported[11] the exclusive γ-sulphenylation of the cyclopentenyl compound (**26**): the anion of the allylic phosphine oxide (**53**) also gave only the γ-sulphenylated



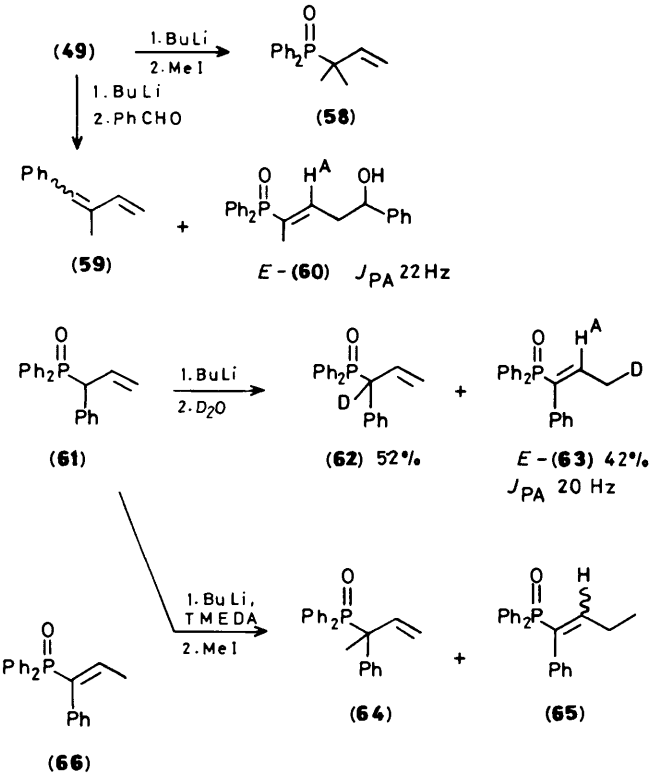
product (**54**). Shift-reagent experiments in the ^1H n.m.r. showed that (**54**) was the *E*-isomer.

We suggest that the vinyl phosphine oxides (**50**), (**52**), and (**54**), like (**36**), result from α-sulphenylation followed by a [1,3]PhS shift,[17] and that the vinyl sulphides (**48**) and (**51**), like (**37**), result from equilibration by proton transfer as PhS is strongly double bond attracting.[22] We confirmed that reprotonation of the anion of (**54**) occurred α to Ph_2PO by treatment of (**54**) with BuLi followed by water. The only product was the vinyl sulphide (**55**).

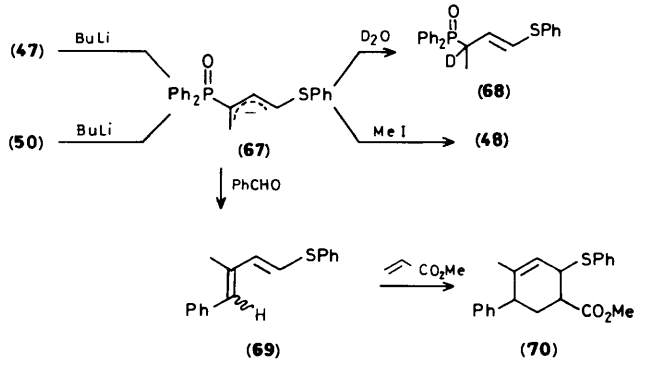
Regioselectivity in Reactions of Anions of Allylic Phosphine Oxides.—We have established that the anions of many allylic phosphine oxides (**56**) react at the α position with carbonyl compounds to give intermediates (**57**) for the Horner-Wittig synthesis of dienes,[10,11,23] but we had studied no examples of (**56**; $R^2 = R^3 = H$), the substitution pattern presumably most susceptible to reaction at the γ position and having the carbon skeleton of (**34**)—(**37**) and (**47**)—(**52**).



The anion of the α-methyl compound (**49**) was deuteriated (D_2O) or methylated [MeI: to give (**58**)] exclusively in the α position, but reacted with PhCHO to give only 16% of the diene (**59**) and 77% of the γ-adduct (**60**) (*E*-isomer only, J_{AP} 22 Hz). The corresponding α-phenyl compound[21] (**61**) gave mixtures of α[(**62**) and (**64**)] and γ[(**63**) and (**65**)] products with D_2O or MeI, and gave no adduct of either sort with PhCHO, only some of the vinyl phosphine oxide (**66**). The tendency for γ reactivity is clearly greater for this substitution pattern and is more marked for carbonyl than for alkyl halide electrophiles.

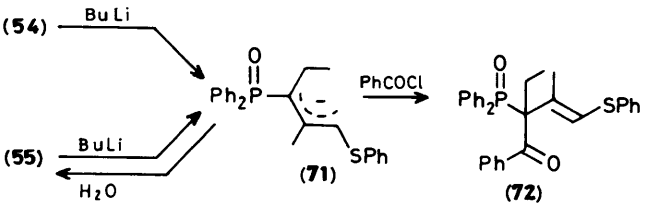


The γ-sulphenylated analogue (**47**) of the α-methyl compound (**49**) gave a deep orange–red anion (**67**) with BuLi in tetrahydrofuran (THF) at −78 °C. Quenching with D_2O or MeI gave the α products (**68**) and (**48**) respectively. Reaction with PhCHO gave the two geometrical isomers of the 1-phenylthiobutadiene (**69**) which gave the Diels–Alder adducts (**70**). In contrast to the reaction of (**49**) with PhCHO, no trace of γ-adduct could be found. The same anion (**67**) was formed from the positional isomer (**50**) so separation of these isomers is unnecessary.



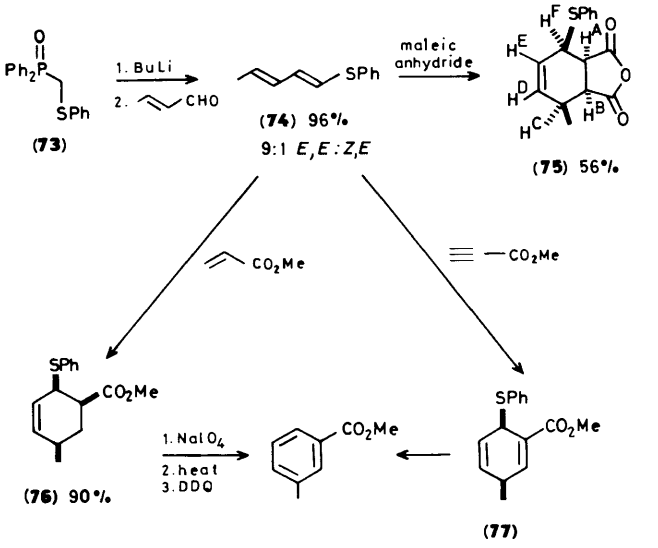
The more highly substituted compounds (**54**) and (**55**) gave a very deep red, almost black, anion (**71**) with BuLi. This anion gave (**55**) with D_2O, but gave only the same vinyl sulphide (**55**) on treatment with PhCHO or Pr^iCHO. It did however react with PhCOCl to give a ketone, tentatively identified as (**72**).

The anion (**67**) reacts at the position α to Ph_2PO and γ to PhS with alkyl halides and with carbonyl compounds. This may be because the lithium derivative of (**49**) reacts α with alkyl halides anyway, and the γ-directing effect[9] of the PhS group reverses this selectivity for (**67**) with carbonyl compounds. An alternative explanation is that the extra stability given to the allyl anion by the PhS group means that it is indeed an anion with



the lithium atom not attached specifically to one carbon atom[24] and that it reacts at the same site (highest HOMO coefficient and highest electron density) with all electrophiles.

Synthesis of 1-*Phenylthiobutadienes.*—The route outlined above, *e.g.* (**49**) to (**47**) + (**50**) to (**69**) gives 1-phenylthiobutadienes providing that the anion reactivity follows the expected pattern. A shorter route combines α-phenylthioalkyl phosphine oxides,[1] *e.g.* (**73**), with enals. 1-Phenylthiopenta-1,3-diene (**74**) is formed in excellent yield by this Horner-Wittig reaction and gave Diels–Alder adducts (**75**), (**76**), and (**77**) whose regioselectivity is dominated by the PhS group.[25] We confirmed this by thermal elimination on the sulphoxide corresponding to the adduct (**76**) and quinone oxidation to methyl *m*-toluate which was also slowly formed from the adduct (**77**) at room temperature, presumably by PhS elimination. The stereochemistry of the maleic anhydride adduct was assigned *endo* (**75**) from its ^1H n.m.r. spectrum made complex by extensive allylic and homoallylic coupling (Table). The couplings AF, BC, and AB all indicate a *cis* arrangement with a dihedral angle *ca.* 0 °C.



Experimental

M.p.s were determined on Reichert hot-stage apparatus and are uncorrected. I.r. spectra were taken on a Perkin-Elmer 257 grating spectrometer; mass spectra on an A.G.I. MS 30 instrument; ^1H n.m.r. spectra were recorded on Perkin-Elmer EM 360 (90 MHz) and EM 360 (60 MHz) in deuteriochloroform solution with $SiMe_4$ or CH_2Cl_2 as internal standard, all spectra are corrected to $SiMe_4$ = 0 p.p.m. Diastereotopic protons are marked with an asterisk.

T.l.c. was carried out on Merck silica gel plates (GF_{254}) and column chromatography was performed on Merck Kiselgel 50, meso 230—400. Solvents were dried and distilled in the usual way, tetrahydrofuran (THF) was freshly distilled from lithium aluminium hydride and diethyl ether from sodium wire. Reactions using alkyl-lithium reagents were carried out under an atmosphere of nitrogen or argon. H.p.l.c. was carried out on

Table. Coupling constants (Hz) in the ^{1}H n.m.r. spectrum of the maleic anhydride adduct (**75**)

B	C	D	E	F	Me	
9	—	—	—	—	—	A
	7.5	—	—	—	—	B
		3.5	3	1.5	8	C
			9	2.5	—	D
				3.5	—	E

a Lichrosort 5160 10 silica gel column (520 × 10 mm) using an Altex model 110A pump and a Cecil Instrument variable wavelength detector (max. injection volume 1 ml, flow rate normally 8—14 ml/min).

1-Phenylsulphinylethyldiphenylphosphine Oxide (**10**; R = Ph).—*m*-Chloroperbenzoic acid (172 mg, 1 mmol) in methylene dichloride (5 ml) was added to a solution of 1-phenylthioethyldiphenylphosphine oxide[1] (**8**) (338 mg, 1 mmol) in THF (1 ml) cooled to −78 °C. The reaction mixture was stirred for 1 h at −78 °C and allowed to warm to room temperature, when it was washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). Removal of the solvents gave a viscous colourless oil which was chromatographed on SiO_2 eluting with EtOAc to give the sulphoxide as a mixture of diasteroisomers (263 mg, 74%) with 20% recovery of the starting phosphine oxide. H.p.l.c. eluting with EtOAc gave the HR_F *isomer*, R_F (EtOAc) 0.33, δ_H 8.15—7.25 (15 H, m, Ph), 3.84 (1 H, quint., J 7.3 Hz, PC*H*Me), and 1.10 (3 H, dd, J_{PH} 14.6, J_{HH} 7.3 Hz, PCH*Me*) (Found: C, 67.3; H, 5.60. $C_{20}H_{19}O_2PS$ requires C, 67.8; H, 5.40%); *m/z* 354 (10% M^+), 229 (25, M − PhSO), 228 (24, M − PhSOH), 201 (75, Ph_2PO), 185 (92, Ph_2P), 126 (21, PhSOH), and 105 (100, C_8H_9) (Found: M^+, 354.0838. $C_{20}H_{19}O_2PS$ requires M, 354.0844), and the LR_F *isomer*, R_F (EtOAc) 0.26, δ_H 8.20—7.20 (15 H, m, Ph), 3.36 (1 H, dq, J_{PH} 12.7, J_{HH} 7.3 Hz, PC*H*Me), and 1.22 (3 H, dd, J_{PH} 14.8, J_{HH} 7.3 Hz, PCH*Me*) (Found: C, 67.74; H, 5.58; P, 8.82. $C_{20}H_{19}O_2PS$ requires C, 67.78; H, 5.40; P, 8.74%); *m/z* 354 (12%, M^+), 228 (85), 227 (60), 201 (65), 185 (50), 126 (48), 104 (48), and 78 (100) (Found: M^+, 354.0845. $C_{20}H_{19}O_2PS$ requires M, 354.0844).

1-Phenylsulphinylpropyldiphenylphosphine oxide. This was similarly prepared as a mixture of diastereoisomers (65%), R_F (EtOAc) 0.28 and 0.19, δ_H 8.3—7.1 (15 H, m, Ph), 4.5—3.4 (1 H, m, PCH), and 2.3—0.7 (5 H, m, Et).

1-Phenylthiovinyldiphenylphosphine Oxide (**5**; R = Ph).—*Method A* (*Pummerer*). Acetic anhydride (225 mg, 2.2 mmol) and methanesulphonic acid (5 drops) were added to a solution of 1-phenylsulphinylethyldiphenylphosphine oxide (642 mg, 1.8 mmol) in methylene dichloride (25 ml) and the mixture was stirred at room temperature for 8 days. The reaction mixture was poured into aqueous sodium carbonate, extracted with methylene dichloride (4 × 30 ml), dried ($MgSO_4$), and the crude product (631 mg) purified by column chromatography on silica eluting with EtOAc to give the vinyl sulphide (399 mg, 65%; 72% based on recovered starting materials), as a viscous colourless oil, R_F (EtOAc) 0.45, δ_H 8.25—7.15 (15 H, m, Ph), 6.16 (1 H, d, J 17.2 Hz, *cis* PC=CH), and 5.63 (1 H, d, J 34.4 Hz, *trans* PC=CH) (Found: C, 71.6; H, 5.30; P, 9.05. $C_{20}H_{17}OPS$ requires C, 71.4; H, 5.10; P, 9.2%); *m/z* 336 (100%, M^+), 277 (42), 227 (15, M − PhSH), 202 (31, Ph_2POH), 201 (62, Ph_2PO), and 123 (42) (Found: M^+, 336.0741. $C_{20}H_{17}OPS$ requires M, 36.0738), $\nu_{max.}$(film) 1 596 (C=C) and 901 cm^{-1} (C=CH_2 deformation).

Method B. Finely powdered *N*-chlorosuccinimide (1.80 g, 13.5 mmol) was added to a solution of 1-phenylthioethyldiphenylphosphine oxide[1] (4.47 g, 13.2 mmol) in carbon tetrachloride (150 ml) and the mixture stirred at 50 °C for 4.5 h until all solid material floated. The reaction mixture was washed with 10% aqueous sodium hydroxide dried ($MgSO_4$), and the solvent removed to give a colourless syrup, shown by ^{1}H n.m.r. to be a mixture of mono- and di-chlorinated derivatives, R_F (EtOAc) 0.60 and 0.50 respectively. The 1-chloro-1-phenylthiophenylphosphine oxide (**14**; R = Ph) (^{1}H n.m.r. shows a doublet at δ 1.73, J 12.5 Hz) so obtained was converted to the required product in two ways. (i) Silica method. Dehydrochlorination readily occurred when small quantities were chromatographed on silica eluting with EtOAc. Larger quantities (> 100 mg) were dissolved in EtOAc and stirred with silica gel (*ca.* 10 g) for 16 h before chromatography. In this way the title compound was obtained as a viscous colourless oil (1.565 g, 66%) from 1-phenylthioethyldiphenylphosphine oxide (2.39 g, 7 mmol) after removal of acetic acid impurity by washing a methylene dichloride solution of the crude product with 10% aqueous sodium hydroxide. 1,2-Dichloro-1-phenylthioethyldiphenylphosphine oxide (0.326 g, 11%) was also isolated from the crude product.

(ii) Zinc bromide method. Zinc bromide (25 mg) was added to a methylene dichloride solution (50 ml) of the intermediate chloro compound from 1-phenylthioethyldiphenylphosphine oxide (4.47 g, 13.2 mmol) and the mixture stirred for 16 h at room temperature. The acidic solution (pH *ca.* 3) was washed with 10% aqueous sodium hydroxide dried ($MgSO_4$), and the vinyl sulphide (2.75 g, 62%) isolated by chromatography on silica eluting with ethyl acetate-10% light petroleum (b.p. 30—40 °C).

1,2-Dichloro-1-phenylthioethyldiphenylphosphine Oxide (**13**; R = Ph). This was isolated during the chromatographic purification above and had R_F (EtOAc) 0.50, δ_H 8.43—8.03 (4 H, m, *o*-ArH), 7.90—7.10 (11 H, m, other ArH), 3.97 (1 H, dd, J_{PH} 14.9 J_{HH} 12.0 Hz, CH_2*Cl), and 3.86 (1 H, dd, J_{PH} 16.5, J_{HH} 12.0 Hz, CH_2*Cl); *m/z* 410 (1%, M^+), 370 (42, M − HCl), 335 (21), 277 (32), 261 (32), 202 (35, Ph_2POH), and 201 (100, Ph_2PO) (Found: M^+, 410.0064. $C_{20}H_{17}Cl_2OPS$ requires M, 410.0064).

1-Methylthiovinyldiphenylphosphine oxide (**5**; R = Me). 1-Methylthioethyldiphenylphosphine oxide[1] (**8**; R = Me) gave the *vinyl sulphide* by method B (dehydrochlorination occurred spontaneously), R_F (EtOAc) 0.31, δ_H 7.88—7.17 (10 H, m, Ph), 6.03 (1 H, d, J_{PH} 18.7 Hz, *cis* PC=CH), 5.64 (1 H, d, J_{PH} 36.2 Hz, *trans* PC=CH), and 2.17 (3 H, s, SMe) (Found: C, 65.1; H, 5.35. $C_{15}H_{15}OPS$ requires C, 65.7; H, 5.50), *m/z* 274 (70%, M^+), 228 (35), 227 (100, M − SMe), 202 (55, Ph_2POH), 201 (60, Ph_2PO), 149 (35), and 125 (35) (Found: M^+, 274.0580. $C_{15}H_{15}OPS$ requires M, 274.0582).

2-Chloro-1-methylthiovinyldiphenylphosphine oxide (**15**). The dichloro compound (**13**; R = Me) (0.28 g) gave the *vinyl chloride* (**15**), by method B(ii) above, as a *ca.* 1:1 mixture of geometrical isomers (84%) separated by chromatography on silica, eluting with EtOAc. The *E*-isomer was an oil, R_F (EtOAc) 0.37, δ_H 8.0—7.25 (10 H, m, Ph), 6.52 (1 H, d, J_{PH} 25.5 Hz, PC=CH), and 2.20 (3 H, s, SMe); *m/z* 308 (12%, M^+), 273 (82, M − Cl), 227 (100), 202 (25, Ph_2POH), 201 (78, Ph_2PO), and 149 (25) (Found: M^+, 308.0195. $C_{15}H_{14}ClOPS$ requires M, 308.0192). The *Z*-isomer was a solid, m.p. 80—81 °C, R_F (EtOAc) 0.46, δ_H 8.0—7.25 (10 H, m, Ph), 7.06 (1 H, d, J_{PH} 11, PC=CH), and 2.14 (3 H, s, SMe); *m/z* 308 (15%, M^+), 273 (100), 227 (90), 202 (27), 201 (49), and 149 (23) (Found: M^+, 308.0201. $C_{15}H_{14}ClOPS$ requires M, 308.0192).

1-Phenylthioprop-1-enyldiphenylphosphine oxide (**17**). This was prepared by method A (76%) from 1-phenylthiopropyldiphenylphosphine oxide[1] (3.52 g, 10 mmol), and by method B(i) (65%) from 4.30 g (12.2 mmol) of the same phosphine oxide, as a mixture of double bond isomers (*ca.* 1:1), R_F (EtOAc) 0.33 and 0.28; δ_H 8.20—6.70 (16 H, m, Ar and vinyl Hz), and 2.20 (dd, J 7.5, 3 Hz), and 2.04 (dd, J 6.5, 3 Hz) (3 H, C=CMe).

Reaction of 1-*Phenylthiovinyldiphenylphosphine Oxide* (**5**; R = Ph) *with Alkyl-lithium Reagents and Electrophiles:* NH_4Cl *as Electrophile.*—1-*Phenylthiopropyldiphenylphosphine oxide* (**19**; R^1 = Me). Methyl-lithium (0.94M solution of the LiBr complex in ether; 1 ml) was added dropwise over 5 min to a solution of 1-phenylthiovinyldiphenylphosphine oxide (239 mg, 0.71 mmol) in THF (8 ml) cooled to −78 °C. The solution went from yellow to orange to dark yellow–green. After 10 min at −78 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl, allowed to warm to room temperature, diluted with water, and extracted with methylene dichloride (3 × 30 ml). The combined extracts were dried ($MgSO_4$) and evaporated and the resulting pale yellow syrup purified by p.l.c. on SiO_2, eluting with EtOAc–20% light petroleum (b.p. 40—60 °C) to give the phosphine oxide[1] (**19**; R^1 = Me) (178 mg, 71%). In the same way the following were prepared.

1-*Phenylthiohexyldiphenylphosphine oxide* (**19**; R^1 = Bu). The vinyl phosphine oxide (**5**; R = Ph) and butyl-lithium gave the *phosphine oxide* (85%) as an oil, R_F (EtOAc) 0.62, δ_H 8.40—6.70 (15 H, m, Ph), 3.55 (1 H, m, PCH), and 2.8—0.5 (11 H, m, other CHs) (Found: M^+, 349.1525. $C_{24}H_{27}OPS$ requires M, 349.1520), m/z 349 (10%, M^+), 285 (M^+ − SPh, 35%), 279 (25%, Ph_3POH), 202 (100%, Ph_2POH), 201 (35%, Ph_2PO), 193 (30%, $PhSC_6H_{12}$), and 123 (50%, $PhSCH_2$).

3-*Methyl*-1-*phenylthiopentyldiphenylphosphine oxide* (**19**; R^1 = Bu^s). The vinyl phosphine oxide (**5**; R = Ph) and s-butyl-lithium gave the phosphine oxide (**19**; R^1 = Bu^s) (72%), as an oil, R_F (EtOAc) 0.55, δ_H 8.10—6.85 (15 H, m, Ph), 3.65 (1 H, dt, PCH), and 2.20—0.65 [11 H, m, including 0.82, (d, J 6 Hz) and other CHs] (Found: M^+, 394.1516. $C_{24}H_{27}OPS$ requires M, 394.1520), m/z 394 (10%, M^+), 324 (20%, Ph_2PCH_2SPh), 284 (20), 20 (100), 201 (40), 193 (28), and 123 (80).

Preparation of Vinyl Sulphides from Reaction of 1-*Phenylthiovinyldiphenylphosphine oxide* (**5**; R = Ph) *with Methyl-Lithium and Aldehydes.*—2-*Methyl*-4-*phenylthiohex*-3-*ene* (**21**; R^1 = Me, R^2 = Pr^i). Methyl-lithium (LiBr complex, 1.45M in ether; 1.5 ml 2.18 mmol) was added to a solution of 1-phenylthiovinyldiphenylphosphine oxide (673 mg, 2 mmol) in THF (10 ml) cooled to −78 °C, and the yellow solution stirred for 15 min. Isobutyraldehyde (216 mg, 0.28 ml, 3 mmol), was then added followed by a further quantity (72 mg, 0.09 ml, 1 mmol) after 5 min in an attempt to quench all the colour. The pale yellow-green solution was allowed to warm slowly to room temperature and after 18 h quenched with saturated aqueous NH_4Cl. The mixture was diluted water and extracted with methylene dichloride (3 × 50 ml). The combined organic extracts were dried ($MgSO_4$), washed with 50% aqueous NaOH and evaporated under reduced pressure to leave a residual yellow–orange oil. This was chromatographed on silica, eluting with CH_2Cl_2 to give the vinyl sulphide (105 mg, 25%) as a colourless oil, R_F (CH_2Cl_2) 0.72, δ_H 7.19 (5 H, br s, Ph), 5.66 (1 H, d, J 10 Hz, vinyl H), 3.08 (1 H, d, sept., J 10, 7 Hz, minor isomer C*H*Me_2), 2.69 (major isomer, C*H*Me_2), 2.27 (2 H, q, J 7.5 Hz, major isomer, CH_2Me), 2.10 (minor isomer CH_2Me), 1.01 (3 H, t, J 7.5 Hz, CH_2*Me*), and 0.97 (6 H, d, J 7 Hz, $CHMe_2$).

A similar reaction gave 1-*phenyl*-2-*phenylthiobut*-1-*ene* (**21**; R^1 = Me, R^2 = Ph) (54%), R_F (CH_2Cl_2) 0.73, two isomers in the ratio 8:1, δ_H 7.80—7.00 (10 H, m, Ph), 6.63 (1 H, s, vinyl H), 2.43 (2 H, q, J 7.2 Hz, CH_2Me), and 1.15 (3 H, t, J 7.2 Hz, CH_2*Me*). The minor isomer has a vinyl signal at δ 6.77 and methylene quartet at δ 2.31.

Preparation of Ketones from Vinyl Sulphides.—1-*Phenylbutan*-2-*one*. The vinyl sulphide (**21**; R^1 = Me, R^2 = Ph) (58 mg, 2.4×10^{-4} mol) was dissolved in deuteriochloroform (2 ml) and water (1 drop) and trifluoroacetic acid (5 drops) were added. The mixture immediately darkened to a deep red–brown and ^{1}H n.m.r. showed the absence of vinyl sulphide. The reaction mixture was dissolved in CH_2Cl_2 (10 ml) and the solution washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated under reduced pressure (< 30 °C). The residual oil was Kugelrohr distilled to give the ketone as a colourless oil (24 mg, 67%), b.p. 110 °C/13 mmHg (lit.,[26] b.p. 230 °C/755 mmHg).

Sulphenylation of Allyldiphenylphosphine Oxide.—Allyldiphenylphosphine oxide (1 g, 4.1 mmol) was treated with butyl-lithium (2.4M, 1.9 ml) and TMEDA (0.65 ml, 4.6 mmol) in THF (30 ml) at −78 °C and then added to a solution of diphenyl disulphide (1 g, 4.6 mmol) in THF (30 ml) at −78 °C, to give a mixture of 1-diphenylphosphinoyl-3-phenylthioprop-1-ene (**36**), 3-diphenylphosphinoyl-1-phenylthioprop-1-ene (**37**), and 1-diphenylphosphinoyl-1-phenylthioprop-1-ene (**35**); m/z 350 (M^+, 70%), 241 (M − PhS, 100), and 201 (Ph_2PO, 80); δ_H 7.9—6.8 (15 H, m, Ph), 6.6—5.8 (1 to 2 H, complex m, vinyl H), 3.40 and 3.24 (*ca.* 1 H, total, each d, J_{HP} 15, J_{HH} 7 Hz, both isomers of PCH_2CH=CS, 37), 3.65 (*ca.* 1 H, dd, J_{HH} 6, J_{HP} 2 Hz, SCH_2C=CP, 36), and 2.02 (1 to 2 H, dd, J_{HH} 6, J_{HP} 2 Hz, *Me*CH=CP 35). In another experiment, the geometrical isomers of (**37**) were separated by column chromatography on silica, eluting with EtOAc. (*Z*)-3-Diphenylphosphinoyl-1-phenylthioprop-1-ene had R_F (EtOAc) 0.29, δ_H 8.10—7.00 (15 H, m, Ph), 6.36 (1 H, br dd, J 9, 3 Hz, C=C*H*SPh), 6.01 (1 H, q, J 7 Hz, CH_2C*H*=C), and 3.35 (2 H, dd, J 15, 7 Hz, PCH_2). The *E*-isomer had R_F (EtOAc) 0.26, δ_H 8.20—6.90 (15 H, m, Ph), 6.50—5.50 (2 H, m, including dd, J 15, 3 Hz, vinyl Hs), and 3.20 (2 H, dd, J 15, 7 Hz, PCH_2).

1-*Diphenylphosphinoyl*-3-*trimethylsilylprop*-1-*ene* (**38**).—This was prepared (86% yield) in a similar way from allyldiphenylphosphine oxide (2.42 g, 10 mmol) and BuLi, quenching with 2 equiv. of trimethylsilyl chloride; it had m.p. 73—74 °C [EtOAc–light petroleum (b.p. 60—80 °C)], R_F (EtOAc) 0.45, δ_H 7.90—7.20 (10 H, m, Ph), 6.71 (1 H, ddt, J 19.3, 16.5, 8.4 Hz, CH_2C*H*=C), 6.04 (1 H, dd, J 24.9, 16.5 Hz, PCH=C), 1.80 (2 H, br d, J 8.4 Hz, CH_2Si), and −0.03 (9 H, s, $SiMe_3$) (Found: C, 68.6; H, 7.25; P, 9.6%. $C_{18}H_{23}OPSi$ requires C, 68.6; H, 7.37; P, 9.95%), m/z 314 (23, M^+), 299 (20, M − Me), 201 (100, Ph_2PO), 77 (42, Ph), and 73 (40, Me_3Si) (Found: M^+, 314.1263. $C_{18}H_{23}OPSi$ requires M, 314.1256).

1-*Diphenylphosphinoyl*-3-*iodoprop*-1-*ene* (**41**). The foregoing phosphine oxide (**38**) and iodine in THF at 0 °C gave the iodo compound (**41**) (29%), δ_H 8.25—7.15 (10 H, m, Ph), 6.70 (1 H, ddt, J_{PH} 17.7, J_{HH} 16.6, 7.2 Hz, PCH=C*H*CH_2), 6.31 (1 H, dd, J_{PH} 21.0, J_{HH} 16.6 Hz, PC*H*=CH), and 3.94 (2 H, d, J 7.2 Hz, $CHCH_2I$), and starting material (27%).

3-*Chloro*-1-*phenylthioprop*-1-*ene* (**42**).—Allyl phenyl sulphide (2.25 g, 15 mmol) was added to a finely powdered suspension of *N*-chlorosuccinimide (2.00 g, 15 mmol) in carbon tetrachloride (40 ml), and the mixture stirred at 3 °C for 24 h. The succinimide was filtered off through Celite and the solvents removed by distillation under reduced pressure below 30 °C. The product was used without further purification; ^{1}H n.m.r. showed it to be almost pure (*E*)-isomer. The chloro sulphide (100%) had δ_H (*E*-isomer) 7.05 (5 H, br s, Ph), 6.16 (1 H, d, J 15 Hz, PhSC*H*=C), 5.47 (1 H, dt, J 15, 7 Hz, CH_2C*H*=CH), and 3.80 (2 H, d, J 7 Hz, CH_2Cl). The (*Z*)-isomer had same spectrum except that CH_2Cl was at δ 3.95.

1-(*Diphenylphosphinoylmethyl*)*oxirane* (**43**).—Hydrogen peroxide solution (85%; 0.06 ml, 2 mmol), trifluoroacetic anhydride (420 mg, 0.28 ml, 2 mmol) and allyldiphenylphosphine oxide (242 mg, 1 mmol) gave the *epoxide* (255 mg, 100%), m.p. 115—117 °C; R_F (EtOAc) 0.23, δ_H 8.20—7.20 (10 H, m, Ph) and 3.60—

2.00 (5 H, two groups of m, aliphatic protons) (Found: C, 69.9; H, 5.85; P, 11.95%. $C_{15}H_{15}O_2P$ requires C, 69.8; H, 5.85; P, 11.99%) (Found: M^+, 258.0806. $C_{15}H_{15}O_2P$ requires M, 258.0809), m/z 202 (100, Ph_2POH), and 201 (98, Ph_2PO).

1-*Diphenylphosphinoyl*-3-*phenylthiopropan*-2-*ol* (**44**).—Butyllithium (1.65M in hexane; 0.1 ml) and thiophenol (1 ml, *ca.* 10 mmol) in THF (5 ml) were added to the above epoxide (258 mg, 1 mmol) in THF (5 ml), to give the *alcohol* (**44**), as an oil (200 mg, 54%), R_F (EtOAc) 0.33, δ_H 7.98—6.95 (15 H, m, Ph), 4.82 (1 H, br s, OH), 4.17 (1 H, m, C*H*OH), 3.07 (2 H, ABX system, J_{AB} 14, $J_{AX} = J_{BX}$ = 6 Hz, CH_2*SPh), and 2.66 (2 H, ABPX system, J_{AB} 15, J_{AP} 11, J_{BP} 9, J_{AX} 9.5, J_{BX} 3 Hz, PCH_2*CH) (Found: M^+, 350.0883. $C_{21}H_{19}OPS$ requires $M - H_2O$ 350.0894), m/z 350 (5%, $M - H_2O$), 241 (100, $M - H_2O$ − PhS), 215 [30, $Ph_2P(O)Me$], and 201 (85, Ph_2PO).

2,3-*Dibromopropyldiphenylphosphine Oxide* (**45**).—(i) *N-Bromosuccinimide*. Finely powdered *N*-bromosuccinimide (180 mg, 1 mmol) was added to a solution of allyldiphenylphosphine oxide (242 mg, 1 mmol) in carbon tetrachloride (25 ml) and, after addition of a few crystals of benzoyl peroxide, the mixture refluxed for 18 h. The reaction mixture was filtered and the residual oil was purified by preparative t.l.c. on silica, eluting with EtOAc, to give the *dibromide* as a gum (135 mg, 33%) which was crystallised and recrystallised from ethyl acetate–hexane; it had m.p. 77—79 °C; R_F (EtOAc) 0.48, δ_H 8.15—6.90 (10 H, m, Ph), 4.60 (1 H, m, C*H*Br), 3.10 (2 H, ABPX system, J_{AB} 15.5, J_{AP} 11.8, J_{BP} 9.7, J_{AX} 7.3, J_{BX} 6.1 Hz, PCH_2*CH), and 3.75 (2 H, distorted d, CH_2Br) (Found: C, 44.5; H, 3.69; Br, 40.4; P, 7.7. $C_{15}H_{15}Br_2OP$ requires: C, 44.8; H, 3.76; Br, 39.8; P, 7.7%) (Found: M^+, 319.9962. $C_{15}H_{14}BrOP$ requires M − HBr, 319.9965), m/z 319 (35%), 201 (100, Ph_2PO), and 77 (35, Ph).

(ii) *Phenyltrimethylammonium perbromide*. The reaction was carried out on 1 mmol scale in THF at room temperature for 18 h. Work-up as above gave the dibromide (**45**) (371 mg, 92%).

(iii) *Bromine*. The reaction was carried out on 10 mmol scale in carbon tetrachloride at room temperature for 20 h. The reaction mixture was dissolved in methylene dichloride, and the solution washed with aqueous sodium thiosulphate, dried ($MgSO_4$), and evaporated. The residual gum was chromatographed on SiO_2, eluting with EtOAc, to give the dibromide (**45**) (3.575 g, 89%).

3-*Bromo*-1-*diphenylphosphinoylprop*-1-*ene* (**46**).—The above brominations also gave the *bromoalkene* (**46**) (29% yield) from the NBS reaction. It was purified by h.p.l.c. on SiO_2, eluting with EtOAc, and had m.p. 116—117 °C, R_F (EtOAc) 0.28, δ_H 8.05—7.10 (10 H, m, Ph), 6.65 (2 H, m, HC=CH), and 4.05 (2 H, dd, J 15, 5 Hz, CH_2Br) (Found: C, 56.5; H, 4.5; Br, 24.5; P, 9.7. $C_{15}H_{14}BrOP$ requires: C, 56.1; H, 4.40; Br, 24.90; P, 9.6%) (Found: M^+, 319.9962. $C_{15}H_{14}BrOP$ requires M, 319.9965), m/z 319 (13% M^+), 241 (55, M − Br), and 201 (52, Ph_2PO).

3-*Diphenylphosphinoyl*-1-*phenylthioprop*-1-*ene* (**37**).—Thiophenol (121 mg, 2.2 mmol), potassium t-butoxide (247 mg, 2.2 mmol) in THF (20 ml), and the above dibromide (**45**) (402 mg, 1 mmol) gave the vinyl sulphide (**47**) (313 mg, 89%) as a 1.2:1 mixture of *Z*:*E* isomers. Sodium hydride and thiophenol gave 62% of (**37**).

3-*Diphenylphosphinoyl*-1-*phenylthiobut*-1-*ene* (**47**).—The anion[1] [BuLi (1.65M in hexane; 3.03 ml) and TMEDA (1.28 g) in THF (30 ml)] of the allyl phosphine oxide (**37**) (78 mg, 2.2×10^{-4} mmol) with methyl iodide (0.15 ml, *ca.* 1.25 mmol) gave the *vinyl sulphide* (**47**) (75%) as a *ca.* 1:1 mixture of *E* and *Z*-isomers, R_F (EtOAc) 0.44 (*Z*) and 0.37 (*E*), separated by column chromatography on SiO_2, eluting with EtOAc–10% light petroleum (b.p. 30—40 °C). The *E*-isomer had δ_H 8.10—6.90 (15 H, m, Ph), 6.17 (1 H, dd, J 15, 3 Hz, PhSC*H*=C), 5.78 (1 H, ddd, J 15, 7, 4.5 Hz, CHC*H*=C), 3.28 (1 H, m, PCH), and 1.32 (3 H, dd, J 16, 7 Hz, PCH*Me*). The *Z*-isomer had δ_H 8.10—6.95 (15 H, m, Ph), 6.20 (1 H, dd, J 9.5, 2 Hz, PhSC*H*=C), 5.90 (1 H, ddd, J 10, 9.5, 6 Hz, CHC*H*=C), 3.74 (1 H, m, PCH), and 1.31 (3 H, dd, J 16, 7 Hz, PCH*Me*).

3-*Diphenylphosphinoyl*-2-*methyl*-1-*phenylthiopent*-2-*ene* (**54**).—The allyl phosphine oxide[11] (**53**) (1 g, 3.5 mmol), butyllithium (2.4M in hexane; 1.6 ml), TMEDA (0.46 ml, 3.8 mmol) in THF (30 ml), and diphenyl disulphide (0.82 g, 3.8 mmol) gave the *allyl sulphide* (1.01 g, 72%) as a colourless oil, R_F (EtOAc) 0.33, $\nu_{max.}$($CHCl_3$) 1 670 (C=C), 1 610, 1 590, 1 490 (Ph), 1 435 (PPh), and 1 170 cm^{-1} (P=O); δ_H 7.2—7.8 (15 H, m, Ph), 3.74 (2 H, s, PhSCH_2), 2.3—1.8 (2 H, m, CH_2C=C), 2.12 (3 H, d, J_{HP} 3 Hz, MeC=CP), and 0.70 (3 H, t, J_{HH} 7 Hz, Me); m/z 392 (M^+, 34%), 359 (M − SH, 18), 315 (M − Ph, 20), 283 (M − PhS, 90), 267 (M − PhS − Me, 22), 201 (Ph_2PO, 100), and 109 (PhS, 80) (Found: M^+, 392.1348. $C_{24}H_{25}OPS$ requires M, 392.1363). Lanthanide shift experiments[11] were performed on this allyl sulphide which confirm the configuration as *E*:

Proton in (**54**)	Chemical shift (δ)	L.I.S. value (p.p.m.)
CH_2SPh	3.7	1.8
*Me*C=CP (*cis*)	2.1	5.8
CH_2CP	*ca.* 2.1	3.8
*Me*CH_2CP	0.7	2.5

These values should be compared with 'average' values for the L.I.S. of protons at different distances from Ph_2PO along an alkyl chain. The L.I.S. values for hexyldiphenylphosphine oxide are given below. The Ph_2PO group binds more weakly to europium than hydroxy, for example, and the L.I.S. values are considerably lower.

	Ph_2PO-CH_2-	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$	$-CH_2-$
L.I.S. value (p.p.m.)	8.0	7.1	1.6	0.2	−0.1	−0.3

3-*Diphenylphosphinoyl*-2-*methyl*-1-*phenylthiopent*-1-*ene* (**55**).—The allyl sulphide (**54**) (1.195 g, 3.05 mmol), butyllithium (2.4M in hexane; 1.4 ml), TMEDA (0.48 ml, 3.4 mmol) in THF (40 ml) at −78 °C, water (1 ml), and aqueous ammonium chloride (30 ml) gave the *vinyl sulphide* (750 mg, 63%) as cream needles, m.p. 173—175 °C, R_F (EtOAc) 0.52, $\nu_{max.}$($CHCl_3$) 1 580, 1 480 (Ph), 1 435 (PPh), and 1 175 cm^{-1} (P=O); δ_H 6.9—8.0 (15 H, m, Ph_2P and PhS), 6.0 (1 H, d, J_{HP} 4 Hz, SC*H*=C–CP), 2.97 (1 H, dd, J_{HP} 9, J_{HH} 6 and 3 Hz, PC*H*CH_2*), 1.5—2.4 (2 H, m, PCHCH_2*Me), overlain by 1.87 (3 H, d, J_{HP} 2 Hz, Me), and 0.90 (3 H, t, J 7 Hz, *Me*CH_2); m/z 392 (M^+, 7%), 283 (M − PhS, 100), 201 (Ph_2PO, 40), and 191 (M − Ph_2PO, 86) (Found: C, 73.1; H, 6.6; P, 7.65. $C_{24}H_{25}OPS$ requires: C, 73.4; H, 6.4; P, 7.9%) (Found: M^+, 392.1353. $C_{24}H_{25}OPS$ requires M, 392.1363).

Benzoylation of 3-*Diphenylphosphinoyl*-2-*methyl*-1-*phenylthiopent*-1-*ene* (**51**).—The vinyl sulphide (**51**) (200 mg, 0.51 mmol), butyl-lithium (0.4 ml, 0.7 mmol), TMEDA (0.1 ml, 0.7 mmol), and benzoyl chloride gave a colourless gum (190 mg, 73%) tentatively identified from its spectra as 3-benzoyl-3-diphenylphosphinoyl-2-methyl-1-phenylthiopent-1-ene (**72**), m/z 496 (M^+, 22%), 387 (M − PhS, 39), 294 (M − Ph_2POH, 28), 201 (Ph_2PO, 100), and 105 (PhCO, 61); δ_H 7.2—8.0 (20 H, m, Ph_2, PhS, and PhC), 5.92 (1 H, s, CH=C), 2.04 (3 H, d, J_{HP} 3 Hz, MeCP), 1.2—1.6 (2 H, m, CH_2*Me), and 0.60 (3 H, t, J 7 Hz, *Me*CH_2).

Phenylsulphenylation of (1-*Methylallyl*)*diphenylphosphine Oxide*.—The phosphine oxide[21] (**49**) (0.5 g, 1.95 mmol), butyl-lithium (1.8M in hexane; 12 ml), TMEDA (0.31 ml, 2.2 mmol) and diphenyl disulphide (480 mg, 2.2 mmol) gave 3-*diphenylphosphinoyl*-1-*phenylthiobut*-2-*ene* (*E*)-(**50**) (219 mg, 31%) as a colourless gum, R_F 0.19 (EtOAc), $\nu_{max.}$($CHCl_3$) 1 625 (C=C), 1 590, 1 480 (PhS), 1 435 (PPh), and 1 165 cm^{-1} (P=O); δ_H 6.2—6.6 (15 H, m, Ph_2P and PhS), 6.20 (1 H, dtq, J_{PH} 20, J_{HH} 8, 1 Hz, SCH_2CH=CP), and 1.73 [3 H, dd, J_{HP} 14, J_{HH} 1 Hz, *Me*C(P)=CH]; *m*/*z* 364 (M^+, 100%), 255 (M − PhS, 93), 201 (Ph_2PO, 48), 185 (Ph_2P, 47), 163 (M − Ph_2PO, 10), 109 (13), and 77 (27) (Found: M^+, 364.1072. $C_{22}H_{21}OPS$ requires M, 364.1051), and 3-*diphenylphosphinoyl*-1-*phenylthiobut*-1-*ene* (*E*)-(**47**) (285 mg, 40%) as a colourless gum, R_F (EtOAc) 0.31, $\nu_{max.}$($CHCl_3$) 1 580, 1 475 (PhS), 1 435 (PPh), and 1 170 cm^{-1} (P=O); δ_H 7.0—7.9 (15 H, m, Ph_2P and PhS), 5.7—6.2 (2 H, m, ABXP system, J_{AB} 15, J_{AP} 4, J_{BX} 7, J_{BP} 5 Hz, SCH^A=CH^B-CH^XP), 3.3 (1 H, m, PCH^X), and 1.36 (3 H, dd, J_{HP} 15, J_{HH} 7 Hz, *Me*CHP); *m*/*z* 364 (M^+, 11%), 255 (M − PhS, 65), 201 (Ph_2PO, 32), 163 (M − Ph_2PO, 100), and 77 (27) (Found: M^+, 364.1038. $C_{22}H_{21}OPS$ requires M, 364.1051). If, after the addition of the anion to the disulphide, a further 1 mol equiv. of butyl-lithium was added, and after 10 min, the reaction quenched with aqueous sodium hydroxide followed by work-up as before, the only product was 3-diphenylphosphinoyl-1-phenylthiobut-1-ene (**47**) (45%).

Methylsulphenylation of (1-*Methylallyl*)*diphenylphosphine Oxide*.—The phosphine oxide (**49**) (0.5 g, 1.95 mmol), butyl-lithium (1.2 ml, 2.2 mmol), TMEDA (0.31 ml, 2.2 mmol), and dimethyl disulphide (0.2 ml, 2.2 mmol) gave 3-*diphenylphosphinoyl*-1-*methylthiobut*-2-*ene* (**52**) (322 mg, 55%), as a colourless gum, R_F (EtOAc) 0.25, $\nu_{max.}$($CHCl_3$) 1 630 (C=C), 1 590, 1 480 (PhS), 1 440 (PPh), and 1 165 cm^{-1}, δ_H 7.3—7.9 (10 H, m, Ph_2P), 6.28 [dtq, J_{HP} 20, J_{HH} 7.5, 1 Hz, CH_2CH=C(Me)P], 3.26 (2 H, dd, J_{HH} 7.5, J_{HP} 2 Hz, SCH_2CH=CP), 2.05 (3 H, s, MeS), and 1.90 (3 H, dd, J_{HP} 13, J_{HH} 1 Hz, *Me*CP); *m*/*z* 302 (M^+, 12%), 287 (M − Me, 27), 256 (M − CH_2S, 100), 201 (Ph_2PO, 90), and 183 (40) (Found: M^+, 302.0905. $C_{17}H_{19}OPS$ requires M, 302.0923).

Deuteriation of (1-*Methylallyl*)*diphenylphosphine Oxide* (**49**).—The allyl phosphine oxide (**49**) (120 mg, 0.47 mmol), butyl-lithium (1.8M in hexane; 0.33 ml, 0.6 mmol) and deuterium oxide (0.1 ml) gave the deuteriated compound, ([1-^{2}H]-1-methylallyl)diphenyl phosphine oxide, as a colourless gum (65 mg, 55%), *m*/*z* 257 (M^+, 12%), 256 (undeuteriated material, 4), 201 (Ph_2PO, 100), and 77 (25); δ_H 7.4—7.9 (10 H, m, Ph), 5.6—6.0 (1 H, m, vinyl H), 4.9—5.2 (2 H, m, CH_2=C) and 1.30 (3 H, d, J_{HP} 16 Hz, Me–CDP).

3-*Diphenylphosphinoyl*-3-*methylbut*-1-*ene* (**58**).—The allyl phosphine oxide (**49**) (500 mg, 1.95 mmol) in dry THF (30 ml), butyl-lithium (1.8M in hexane; 1.2 ml) and TMEDA (0.30 ml, 2.1 mmol) at −78 °C and methyl iodide gave pale yellow crystals of the allyl phosphine oxide (360 mg, 68%), m.p. 120—122 °C (lit.,[27] 105—106 °C) [from benzene–light petroleum (b.p. 60—80 °C)], R_F (EtOAc) 0.26, *m*/*z* 270 (M^+, 22%), 202 (Ph_2POH, 100), 162 (40), and 91 (40); δ_H 7.3—8.1 (10 H, m, Ph_2P), 6.00 [1 H, ddd, J_{HH} (*cis*) 11, J_{HH} (*trans*) 18, J_{HP} 7 Hz, $PCCH$=CH_2], 5.24 [1 H, ddd, J_{HH} (*cis*) 11, J_{HH} (*gem*) 4, J_{HP} 1 Hz, PCCH=CH*H*], 5.09 [1H, ddd, J_{HH} (*cis*) 11, J_{HH} (*gem*) 4, J_{HP} 1 Hz, PCCH=C*H*H], and 1.33 (6 H, d, J_{HP} 14 Hz, Me_2CP).

The Reaction of (1-*Methylallyl*)*diphenylphosphine Oxide* (**49**) *with Benzaldehyde*.—The allylphosphine oxide (0.8 g, 3.1 mmol) was treated with butyl-lithium (1.8M in hexane; 1.9 ml) at −78 °C in THF (30 ml) for 0.3 h. The deep red anion was quenched with benzaldehyde and allowed to warm to room temperature for 2 h. The pale yellow solution (with its white precipitate) was treated with aqueous ammonium chloride and extracted with chloroform (3 × 30 ml). The chloroform was dried ($MgSO_4$) and evaporated to give a pale yellow oil. Column chromatography, eluting first with dichloromethane, then with ethyl acetate, gave 2-methyl-1-phenylbutadiene (**59**) (71 mg, 16%) as a colourless oil, R_F (CH_2Cl_2) 0.76, δ_H 7.3 (5 H, m, Ph), 6.55 (1 H, dd, *J* 10, 18 Hz, *CH*=CH_2), 6.52 (1 H, s, PhC*H*=C), 5.29 (1 H, d, *J* 18 Hz, CH=C*HH*), 5.12 (1 H, d, *J* 10 Hz, CH=C*HH*), and 2.00 (3 H, s, MeC=C); *m*/*z* 144 (M^+, 38%) and 129 (M − Me, 100), and the γ-adduct, 4-*diphenylphosphinoyl*-1-*phenylpent*-3-*en*-1-*ol* (**60**) (873 mg, 77%) as a white foam, R_F (EtOAc) 0.12, *m*/*z* 344 (M^+ − H_2O, 9%), 256 (M − PhCHO, 100), and 201 (Ph_2PO, 57%); δ_H 7.2—7.6 (15 H, m, Ph_2P and PhC), 6.12 [1 H, dt, J_{HP} 22 (*cis*), J_{HH} 7 Hz, PC=C*H*CH_2], 5.27 (1 H, br s, OH), 4.68 (1 H, t, *J* 6 Hz, OC*H*CH_2), 2.65 (2 H *J*, m, $CHCH_2CH$=), and 1.82 (3 H, d, *J* 12 Hz, Me–CP); $\nu_{max.}$($CHCl_3$) 3 300 (OH), 1 630 (C=C), 1 600, 1 490 (Ph), 1 435 (PPh), and 1 160 cm^{-1} (P=O). When the reaction was repeated using TMEDA as co-solvent, the allyl phosphine oxide (**49**) (0.8 g, 3.1 mmol), gave the diene (**59**) (69 mg, 15%), and the γ-adduct *E*-(**60**) (780 mg, 69%).

Deuteriation of 3-*Diphenylphosphinoyl*-1-*phenylthiobut*-1-*ene* (**47**).—The allylphosphine oxide (**47**) (70 mg, 0.19 mmol), butyl-lithium (1.8M in hexane; 0.12 ml) in the THF (30 ml) at −78 °C and deuterium oxide (0.1 ml) gave [3-^{2}H]-3-diphenylphosphinoyl-1-phenylthiobut-1-ene (**68**) (47 mg, 67%) as a colourless oil, R_F (EtOAc) 0.35, δ_H 7.0—8.0 (15 H, m, Ph_2P and PhS), 5.8—6.2 [2 H, ABP system, J_{HH} (*trans*) 15, J_{AP} 4, J_{BP} 5 Hz, $PCCH^B$=CH^AS], and 1.32 (3 H, d, J_{HP} 15 Hz, MeCDP); *m*/*z* 365 (M^+, 10%), 256 (M − PhS, 95), 201 (Ph_2PO, 100), and 164 (M − Ph_2PO, 89).

3-*Diphenylphosphinoyl*-3-*methyl*-1-*phenylthiobut*-1-*ene* (**48**).—The sulphenylated phosphine oxide (**47**) (116 mg, 0.32 mmol), butyl-lithium (1.8M in hexane; 0.2 ml), and TMEDA (0.05 ml, 0.36 mmol) in dry THF (30 ml) with methyl iodide gave the *methylated product* (**48**) (60 mg, 50%), R_F (EtOAc) 0.24, $\nu_{max.}$($CHCl_3$) 1 580, 1 480 (PhS), 1 440 (PPh), and 1 170, cm^{-1} (P=O); δ_H 7.4—8.1 (10 H, m, Ph_2P), 7.31 (5 H, s, PhS), 6.19 [1 H, dd, J_{HH} 15 (*trans*), J_{HP} 3 Hz, SCH=CHCP], 5.92 (1 H, dd, J_{HH} 15, J_{HP} 5 Hz, SCH=C*H*CP), and 1.36 (6 H, d, J_{HP} 15 Hz. Me_2CP); *m*/*z* 378 (M^+, 3.5%), 269 (M − PhS, 80), 201 (Ph_2PO, 60), and 177 (M − Ph_2PO, 100) (Found: M^+, 378.1213. $C_{23}H_{23}OPS$ requires M, 378.1206).

2-*Methyl*-1-*phenyl*-4-*phenylthiobutadiene* (**69**).—The sulphenylated allyl phosphine oxide (**47**) (632 (mg, 1.75 mmol) was treated with butyl-lithium (1.8M in hexane; 1.1 ml) and TMEDA (0.27 ml, 1.9 mmol) in dry THF (30 ml) at −78 °C. After 0.2 h, the deep red-orange anion was quenched with benzaldehyde (0.19 ml, 1.9 mmol) and allowed to warm to room temperature. After 0.5 h, the pale yellow–brown cloudy solution was treated with aqueous ammonium chloride (30 ml) and extracted with chloroform (3 × 30 ml) The combined organic extracts were washed with dilute hydrochloric acid (20 ml) and saturated brine (20 ml), dried ($MgSO_4$), and evaporated to give a pale red oil. Purification by chromatography on SiO_2, eluting with CH_2Cl_2, gave the *diene* (**69**) (298 mg, 68%) as an oil, R_F (CH_2Cl_2) 0.80, $\nu_{max.}$(film) 1 665, 1 600 (C=C), 1 590, 1 490, and 1 480 cm^{-1} (Ph); δ_H 7.2—7.4 (10 H, m, Ph and PhS), 6.4—7.0 (3 H, complex m, vinyl H), and 2.15 and 2.04 (3 H, two d, each *J* 1 Hz, ratio 1:17, both isomers of *Me*C=CH); *m*/*z* 252 (M^+, 12%), 218 (43), 143 (M − PhS, 35), 140 (100), and 109 (PhS, 80) (Found: M^+, 252.0958. $C_{17}H_{16}S$ requires M, 252.0971). Similarly, the sulphenylated allyl phosphine oxide (**50**) (592 mg,

1.6 mmol), butyl-lithium (1.8M in hexane; 1 ml), TMEDA (0.25 ml, 1.8 mmol), and benzaldehyde (0.18 ml, 1.8 mmol) gave the same diene (230 mg, 58%).

Diels–Alder Reaction of 2-Methyl-1-phenyl-4-phenylthiobutadiene with Methyl Acrylate.—The diene (**69**) (230 mg, 0.92 mmol) was heated with methyl acrylate (0.45 ml, 5 mmol), benzene (2 ml), and a trace of hydroquinone in a sealed tube at 140 °C for 41 h. The pale orange liquid was purified by column chromatography on SiO_2, eluting with CH_2Cl_2, to give the Diels–Alder adduct (**70**) (145 mg, 47%) as a colourless oil, δ_H 7.0—7.6 (10 H, m, PhS and Ph), 6.7—7.0 (small m, vinyl H), 5.6—6.0 (small m, vinyl H), 4.1—4.3 (1 H, m, PhSC*H*), 3.28 and 3.64 (3 H, s, MeO), and 1.4—3.2 (complex m, MeC= and ring protons); *m/z* 338 (M^+, 9%), 229 (M − PhS, 80), 169 (M − PhSH − CO_2Me, 100), and 110 (PhSH, 15) (Found: M^+, 338.1337. $C_{21}H_{22}O_2S$ requires M, 338.1339).

Deuteriation of (1-Phenylallyl)diphenylphosphine Oxide (**61**).—The allylphosphine oxide (**61**) (250 mg, 0.79 mmol), butyl-lithium (1.8M in hexane; 0.56 ml) and deuterium oxide (0.1 ml) gave deuteriated starting material (**62**) (130 mg, 52%) as a crystalline solid, R_F (EtOAc) 0.43, δ_H 7.1—8.0 (15 H, m, Ph_2P, PhC), 6.1—6.4 (1 H, m, vinyl H), 4.9—5.2 (2 H, m, CH_2=C), and 4.2 (<0.1 H, t, J 8 Hz, CHP undeuteriated material); *m/z* 319 (M^+, 14%) and 201 (Ph_2PO, 100), and the residue, after preparative t.l.c., gave [1-^{2}H]-3-diphenylphosphinoyl-3-phenylprop-2-ene (**63**) as a colourless oil (108 mg, 42%), R_F (EtOAc) 0.29, δ_H 7.0—7.8 (15 H, m, Ph_2P and PhC), 6.72 (1 H, dt, J_{HP} 20, J_{HH} 6 Hz, PC=C*H*CH_2), and 1.75 (2 H, dd, J_{HH} 6, J_{HP} 3 Hz, DCH_2CH=CP); *m/z* 319 (M^+, 80%, 318 (undeuteriated material, 100%), and 201 (Ph_2PO, 25).

Methylation of (1-Phenylallyl)diphenylphosphine Oxide (**61**).—The allylphosphine oxide (**61**) (500 mg, 1.6 mmol), TMEDA (0.25 ml, 1.8 mmol), butyl-lithium (1.8M in hexane; 1 ml) and methyl iodide (0.11 ml, 1.8 mmol) gave a mixture of methylated products (361 mg, 69%) [from light petroleum (b.p. 40—60 °C)], identified from their n.m.r. spectra as the mixture of α- and γ-adducts (**64**) and (**65**), δ_H 6.8—7.9 (15 H, m, Ph_2P, and PhC), 6.4—6.8 (1 H, m, vinyl H from PCC*H*=C and PC–CH), 5.1—5.5 (2 H, of one isomer, m, PCC–CH_2), 2.10 (2 H, of one isomer, quint., J_{HP} 3, J_{HH} 8 Hz, MeCH_2CH=CP, 1.72 (3 H, of one isomer, d, J_{HP} 15 Hz, MeCP), and 0.98 (3 H, of one isomer, t, J 8 Hz, *Me*CH_2C=).

1-Phenylthiopenta-1,3-diene (**74**).—Phenylthiomethyldiphenylphosphine oxide[1] (**73**) (2 g, 6.2 mmol) was treated with butyl-lithium (1.8M in hexane; 3.8 ml) in dry THF (30 ml) at −78 °C for 0.3 h. The orange anion was quenched with crotonaldehyde and the reaction mixture allowed to warm to room temperature for 0.6 h, to give a thick white precipitate. Aqueous ammonium chloride (30 ml) was added, and the mixture was extracted with chloroform (3 × 30 ml). The combined chloroform extracts were dried ($MgSO_4$) and evaporated to give an oil, which was purified by column chromatography on SiO_2, eluting with CH_2Cl_2, to give the *dienyl sulphide* (**74**) (1.06 g, 96%), as a colourless oil, R_F (CH_2Cl_2) 0.79, $\nu_{max.}$(film) 1 640 (C=C), 1 580, and 1 480 cm^{-1} (Ph); δ_H 7.1—7.4 (5 H, m, Ph), 5.4—6.6 (4 H, m, vinyl protons), and 1.77—1.73 (3 H, 2 d, J 6 Hz ratio 9:1, MeC=C); *m/z* 176 (M^+, 100%), 161 (M − Me, 15), 110 (PhSH, 25), and 99 (M − Ph, 62) (Found: M^+, 176.0658. $C_{11}H_{12}S$ requires M, 176.0658).

6-Methyl-3-phenylthiocyclohex-4-ene-1,2-dicarboxylic Anhydride (**75**).—The diene (**74**) (354 mg, 2.02 mmol) and maleic anhydride (400 mg, 4 mmol) were heated under reflux in dry xylene (15 ml) under nitrogen for 17 h, to give a pale yellow solution. Removal of the solvent and crystallisation of the residue from ethyl acetate–light petroleum (b.p. 60—80 °C) gave the *cyclic anhydride* (310 mg, 56%) as pale yellow needles, m.p. 112—115 °C, R_F (CH_2Cl_2) 0.56, $\nu_{max.}$($CHCl_3$) 1 845, 1 775 (C=O), 1 560, and 1 480 cm^{-1} (Ph); δ_H 7.2—7.5 (5 H, m, PhS), 6.10 (1 H, ddd, H^D), 5.83 (1 H, ddd, H^E), 3.84 (1 H, dddd, H^F), 3.67 (1 H, dd, H^A), 3.37 (1 H, dd, H^B), 2.60 (1 H, m, H^C), and 1.44 (3 H, d, J 8 Hz, *Me*CH^C); *m/z* 274 (M^+, 20%), 164 (M − maleic anhydride, 8), 110 (PhSH, 100), 93 (40), 91 (27), and 77 (28) (Found: M^+, 274.0671. $C_{15}H_{14}O_3S$ requires M, 274.0662).

Methyl 5-Methyl-2-phenylthiocyclohex-3-ene-1-carboxylate (**76**).—The diene (**74**) (630 mg, 3.6 mmol), methyl acrylate (1.8 ml, 20 mmol), and benzene (3 ml) were heated with a small amount of hydroquinone in a sealed tube at 150 °C for 17 h. The solvent was evaporated and the pale yellow residue was purified by column chromatography on SiO_2, eluting with acetone–light petroleum (b.p. 60—80 °C) (3:7) to give the *ester* (**76**) (853 mg, 90%) as a colourless oil, R_F [acetone–light petroleum (b.p. 60—80 °C) (3:7)] 0.63 and 0.57 (two diastereoisomers), $\nu_{max.}$(film) 1 730 (C=C), 1 580, and 1 480 cm^{-1} (PhS); δ_H 7.1—7.5 (5 H, m, PhS), 5.6—6.0 (2 H, m, vinyl H), 4.2 (1 H, m, PhSC*H*), 3.69 and 3.32 (3 H, two s, CO_2Me), 1.5—3.1 (4 H, m, $CHCH_2CHCO_2Me$), and 0.99 and 0.97 (3 H, two d, J 6 Hz, *Me*CH), *m/z* 262 (M^+, 20%), 238 (57), 195 (90), 153 (80, M − PhS), 136 (60), and 109 (PhS, 100) (Found: M^+, 262.1026. $C_{10}H_{18}O_2S$ requires M, 262.1027).

Aromatisation of the Adduct (**76**).—The sulphide (**76**) (580 mg, 2.2 mmol) was oxidised with sodium metaperiodate (535 mg, 2.56 mmol) in methanol (15 ml) and water (7 ml) at room temperature for 18 h. The dark oil was purified by preparative t.l.c. on SiO_2, eluting with CH_2Cl_2, the band at R_F 0.8 being identified as diphenyl disulphide (68 mg) and that at 0.6 being the aromatised product (213 mg, 65%). The n.m.r. of the lower fraction showed the presence of methyl *meta*-toluate, δ_H 7.8 (1 H, m, *ortho*-H), 7.3 (3 H, m, other ArHs), 3.85 (3 H, s, MeO), and 2.35 (3 H, s, Me).

Reaction of 1-Phenylthiopenta-1,3-diene with Methyl Propiolate.—The diene (**74**) (790 mg, 4.5 mmol) was heated with methyl propiolate (1 ml, 2.5 mmol) and benzene (2 ml) and a trace of hydroquinone in a sealed tube at 140 °C for 17 h. The pale orange liquid was purified by column chromatography on SiO_2, eluting with CH_2Cl_2, to give a pale yellow oil (482 mg, 41%), $\nu_{max.}$(film) (taken immediately) 1 720 (C=O), 1 670, 1 630 (C=C), 1 585, 1 480 (PhS), and 1 250 cm^{-1} (MeO); after 1 week at room temperature, the product was converted entirely into methyl *m*-toluate.

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