Migration of the Diphenylphosphinoyl Group in Competition with the Phenylthio-, Methylthio-, or Methoxy-groups from the same Migration Origin

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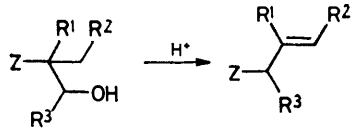
When both functional groups are present at the same migration origin, Ph_2PO migrates in preference to MeO. Either Ph_2PO or RS may migrate depending on the substituents at the migration terminus. Fragmentation reactions compete with rearrangement in both cases. ^{13}C N.m.r. spectra of reactants and products are reported.

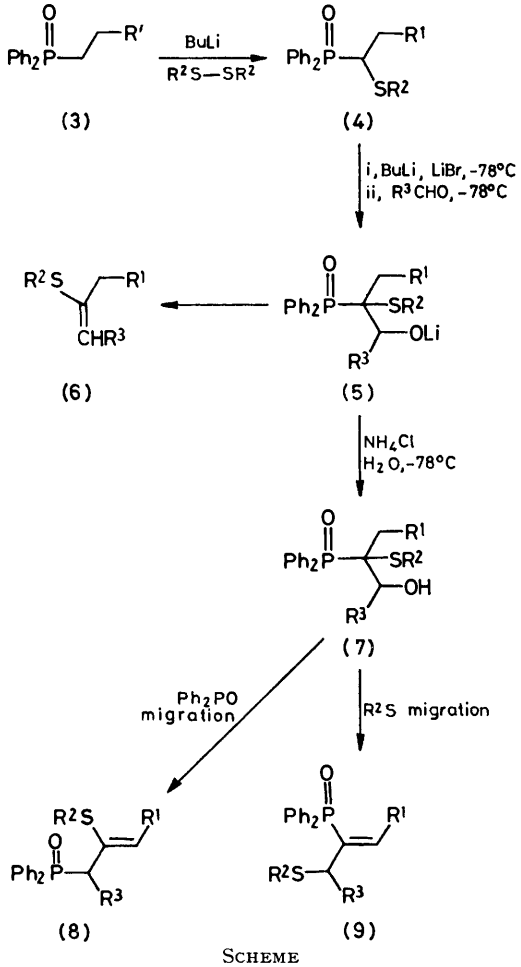
PHENYLTHIO [1] and diphenylphosphinoyl [2] groups migrate in preference to alkyl groups during the acid-catalysed rearrangement of alcohols (1).[3] The allyl sulphide (2;



(1) (2)

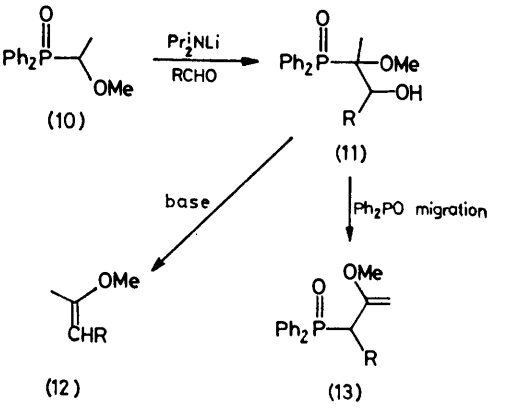
Z = PhS, Ph_2PO

Z = PhS) or phosphine oxide (2; Z = Ph_2PO) products form useful anions for organic synthesis.[1-3]

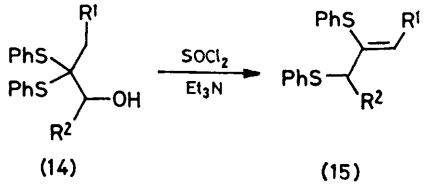


(3) (4) (6) (5) (7) (8) (9)

SCHEME



(10) (11) (12) (13)



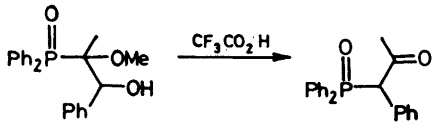
(14) (15)

SCHEME (*Continued*)

Recently we studied compounds with both functional groups at the same migration origin (see Scheme), the sulphenylated phosphine oxides (4), using them in a synthesis of vinyl sulphides (6).[4,5] We also studied the methoxy analogues (11), using them in a synthesis of vinyl ethers (12).[6] Parallel with this work we studied the chemistry of the bis(phenylthio)acetals (14), including their rearrangement to give (15).[4,7] We now report on our investigation into similar rearrangement reactions on adducts (7) and (11). We hoped to find the products of Ph_2PO migration (8) and (13) since these are allylphosphine oxides containing potential ketones. We argued that the MeO group in (11) and, to a lesser extent, the R^2S group in (7) might assist Ph_2PO migration whereas the Ph_2PO group might suppress MeO or R^2S migration.

Ph_2PO vs. MeO *Migration*.—The benzaldehyde adduct (11; R = Ph) of 1-methoxyethyldiphenylphosphine oxide (10) [6] rearranged in trifluoroacetic acid (TFA), conditions we used for simple benzaldehyde adducts (1; Z = Ph_2PO, R^3 = Ph),[2] with Ph_2PO migration to give the ketone (16) in 93% yield. No alkanal adducts

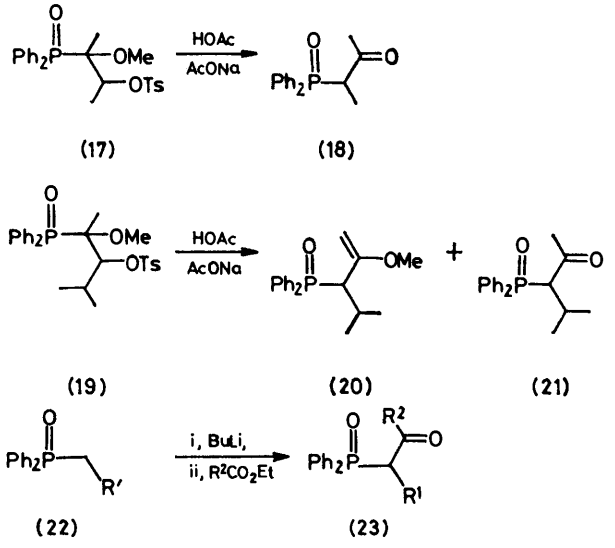
would rearrange cleanly under these or other acidic conditions, nor were we able to isolate the vinyl ether (13; R = Ph) from the TFA reaction. The problem seemed to be fragmentation—always a threat in rearrangement reactions [8]—caused by protonation at



(11; R = Ph) (16)

OMe or PO. We therefore returned to our original method [9] for bringing about Ph_2PO migration—the rearrangement of the tosylates of (11).

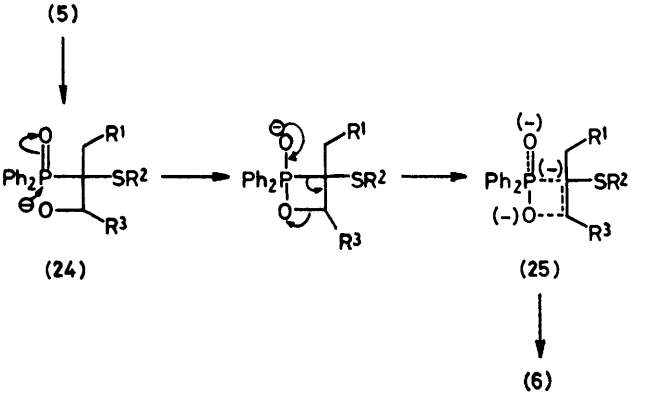
The acetaldehyde adduct (11; R = Me) gave the tosylate (17) which rearranged in buffered acetic acid, presumably by Ph_2PO migration, to give the ketone (18) in 83% yield. With the tosylate of the isobutyraldehyde adduct (19) we finally found some rearranged vinyl ether * (20) but the ketone (21) was formed too. We could convert the product mixture entirely into the ketone (21) ($HCl–H_2O$–THF), in a total yield of 65%, but not into the vinyl ether (20). We had meanwhile found that we could make the ketones (23) in one step



by direct acylation of simple phosphine oxides (22).[10] The more complicated rearrangement route, though mechanistically interesting, is therefore unlikely to be of any importance in synthesis.

Ph_2PO vs. RS *Migration: Preparation of the Alcohols* (7).—The starting materials (4; R^2 = Ph or Me) are readily available from the sulphenylation [5] of the phosphine oxides (3) with diphenyl or dimethyl disulphide (see Scheme). Our first attempts to make the adducts (5) gave only the vinyl sulphides (6) by completion of the Horner–Wittig reaction. This is because the sulphur atom accelerates the elimination of diphenylphosphinate ion from the intermediate (24) by stabilising the partial negative charge on the α-carbon atom in the transition state (25).[5]

However, by carrying out anion formation on (4), addition of the aldehyde, and part of the work-up at −78 °C, we were able to isolate the alcohols (7). The orange-red lithium derivatives of the sulphenylated phosphine oxides (4) were formed with n-butyl-lithium (BuLi) in tetrahydrofuran (THF) saturated with anhydrous lithium bromide (known to retard the final stage of the Wittig reaction [11]) at −78 °C. The aldehyde was



added at this temperature, and as soon as the colour had disappeared, the reaction was quenched with aqueous ammonium chloride solution, and only then allowed to come to room temperature. In this way the alcohols (7) could be isolated in up to 90% yield (Table 1), and separated into crystalline diastereoisomers by evaporation and column chromatography. Yields with R^2 = Me were consistently higher than with R^2 = Ph: this may be because steric crowding in (5) favours the second stage of the Horner–Wittig reaction. However, with R^2 = Ph stereoselectivity was higher, and only one diastereoisomer was isolated.

Stereochemistry of the Alcohols (7).—The two diastereoisomers designated HR_F (faster running) or LR_F (slower running) in Table 1 from their t.l.c. behaviour gave distinct n.m.r. spectra. In all cases the signals for the aromatic protons in the Ph_2PO group were different for the two isomers. In the LR_F isomer we observed the normal pattern [2] of a narrow multiplet (width at half height *ca.* 20 Hz) at *ca.* τ 2.5 for the *m* and *p* protons and a broader multiplet (width at half height *ca.* 50 Hz) at *ca.* τ 2.0 for the *o*-protons. The HR_F isomer showed a similar signal for the *m* and *p* protons but the *o*-protons appeared consistently as two multiplets of equal intensity, one at τ 2.0 and one at *ca.* τ 1.5.

The enhanced diastereotopicity of the *o*-protons in the HR_F isomer may result from steric crowding as we have observed the same effect in alkyl and allyl phosphine oxides with larger substituents.[12] Steric crowding is probably also responsible for the consistent appearance of the signal for MeS in (7; R^2 = Me) at *ca.* 0.5 Hz higher field in the HR_F isomer. We have observed the same effects in the methoxy-compounds (26) where the

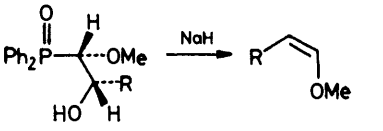
* Phosphonate esters of this type have been made by G. Sturtz, *Bull. Soc. chim. France*, 1964, 2340.

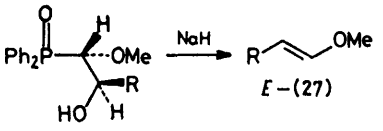
TABLE 1

Adducts (7) from sulphenylated phosphine oxides and aldehydes

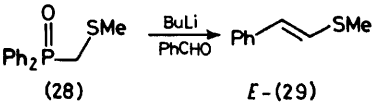
Entry	R^1	R^2	R^3	Yield (7) %	Isomer ratio $HR_F : LR_F$ [a]
1	H	Me	Me	64	42 : 22
2	Me	Me	Me	79	55 : 24
3	Me	Me	Ph	90	4 : 1
4	Me	Ph	Me	62	*b*
5	Me	Ph	Ph	70	*b*
6	Me	Ph	Ph	36 [c]	*b*

[a] See text. [b] Only one diastereoisomer isolated. [c] Without LiBr.

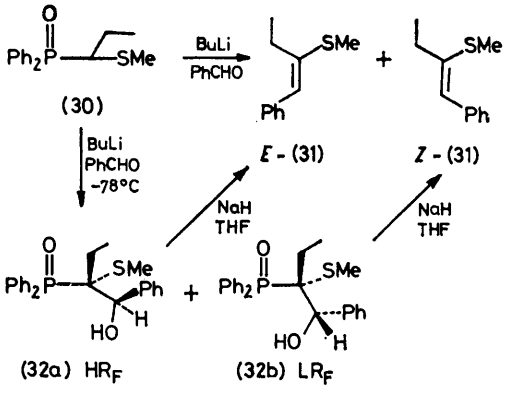




LR_F isomer (26a) gives the *Z*- and the HR_F isomer the *E*-vinyl ether (27).[6] We have now similarly correlated the structures of the isomers of (7) with those of the vinyl sulphides (6) produced from them.



The one-step procedure [5] from (28) and benzaldehyde gives the known vinyl sulphide (29) with an *E* : *Z* ratio of *ca.* 20 : 1. By contrast the simple Wittig route, using the phosphonium salt, gives an *E* : *Z* ratio of 53 : 47.[13]

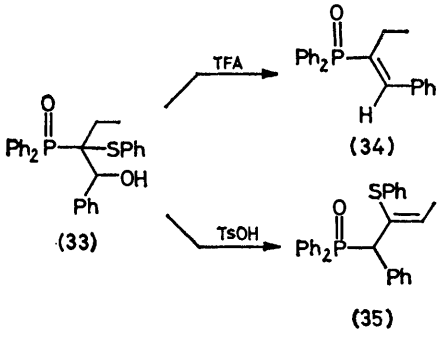


With an extra ethyl group in the molecule (30) the one-step procedure [5] gave an *E* : *Z* ratio in the product (31) of 4 : 1. The low-temperature procedure gave the two diastereoisomers (32a) and (32b) in the same ratio (4 : 1, see entry 3, Table 1). Both diastereoisomers gave the vinyl sulphide on treatment with NaH in THF, the LR_F isomer gave only *Z*-(31), and the HR_F isomer gave an *E* : *Z* ratio of 10.1. We therefore assign the configurations (32a) to the HR_F and (32b) to the LR_F isomers respectively.

The same series of experiments with the corresponding PhS compounds gave similar results. The one-step procedure [5] gave *E* : *Z* (6; R^1 = Me, R^2 = R^3 = Ph) in a 4 : 3 ratio. The two-step procedure gave a mixture of diastereoisomers (5 : 1, $HR_F : LR_F$) of (7) which was not separated but treated with NaH in THF to give a 5 : 1 ratio of *E* : *Z* (6; R^1 = Me, R^2 = R^3 = Ph). Again, the HR_F isomer gave the *E*-vinyl sulphide.

Since the n.m.r. spectra are consistent across the whole range of adducts (7) and (11) we assign the configuration (*SS*, *RR*) to the LR_F isomers which give the *Z*-vinyl ethers or sulphides, and the configuration (*SR*, *RS*) to the HR_F isomers which give the *E*-vinyl ethers or sulphides on base-catalysed elimination of $Ph_2PO_2^-$.

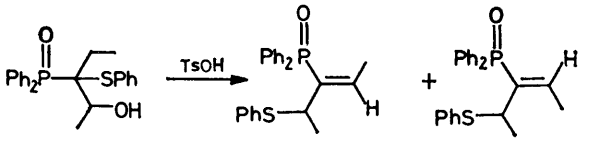
Rearrangement of the Alcohols (7).—The first compounds we attempted to rearrange were adducts of the phenylthio-compound (4; R^1 = Me, R^2 = Ph) with acetaldehyde and benzaldehyde. In TFA at room temperature, the benzaldehyde adduct (33) loses PhSOH to give the vinyl phosphine oxide (34) with a characteristic [14] *cis* vicinal coupling constant (J_{HP} 22 Hz) between the vinyl proton and the phosphorus atom. Some bis(phenylthio)-compounds (1; Z = R^1 = PhS) also lose PhSOH in TFA. With TsOH in toluene under reflux the benzaldehyde adduct (33) gave traces of (34), some diphenyl disulphide, and a crystalline rearranged product in 50% yield whose structure later turned out to be (35), the product of Ph_2PO migration. At the time it was difficult to decide between structures (35) and (9; R^1 = Me, R^2 = R^3 = Ph) for this product.



The acetaldehyde adduct (36) gave both geometrical isomers of the product of PhS migration (37), which were separated with difficulty by p.l.c. Each had a double quartet for its vinyl proton in its n.m.r. spectrum with characteristic [14] *trans* J_{PH} of 37 Hz for *Z*-(37) and *cis* J_{PH} of 22 Hz for *E*-(37). The absence of these signals provided negative evidence for the structure of (35) but confirmation of both structures came from their mass spectra, and particularly the ^{13}C n.m.r. spectra.

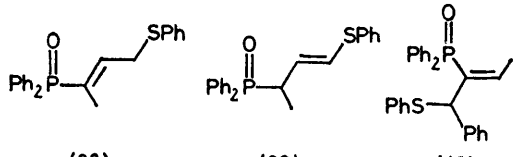
In the mass spectrometer, both allyl and vinyl sulphides *e.g.* (38) and (39) [15] lose PhS very rapidly, but

loss of Ph_2PO is characteristic of allyl rather than vinyl phosphine oxides. Thus the mass spectrum of (38) has only a weak peak at *m/e* 163 for $M - Ph_2PO$ while this is the base peak for (39).



(36) *Z*-(37) *E*-(37)

Both (35) and (37) also lose PhS in the mass spectrometer, but only (35) shows $M - Ph_2PO$, suggesting that (35) is the allyl and (37) the vinyl phosphine oxide. All



(38) (39) (40)

compounds show a fragment ion for Ph_2PO^+ or $Ph_2POH^{+\cdot}$; the distinguishing fragment is $M - Ph_2PO$. (Table 2).

TABLE 2

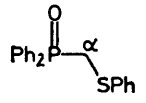
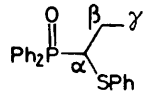
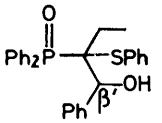
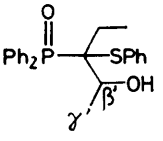
Mass spectra of (35), (37), (38), and (39)

Compound	M^+	M − PhS	$M - Ph_2PO$	Others	$Ph_2PO(H)$
(35)	440(27)	331(100)	238(85)	311(32)	202(100)
(37)	378(35)	269(55)		345(23)	201(100)
(38)	364(100)	255(93)	163(10)		201(48)
(39)	364(11)	255(65)	163(100)		201(32)

Though some ^{13}C spectra of phosphine oxides and sulphides have been reported,[16,17] none are for compounds also containing RS groups. We therefore used the starting materials for these experiments (Table 3) to establish characteristic chemical shifts and ^{13}C–^{31}P coupling constants for these compounds. From these and other data [18] we have drawn up a table (Table 4) of approximate shielding effects of PhS and Ph_2PO in various compounds.

TABLE 3

^{13}C N.m.r. spectra of sulphenylated phosphine oxides

Compound	Chemical shift (p.p.m. downfield from $SiMe_4$) and ^{13}C–^{31}P coupling constant (Hz) in parentheses, for carbons α, β, or γ to phosphorus		
	α	β	γ
	34.0(68)		
	52.8(70)	23.2 [a]	12.5(10)
	55.3(64)	26.1 [a] 80.9(2.5)β′	12.8(3.5)
	59.9(86)	28.4 [a] 69.8 [a]β′	9.5(4.0) 19.3(7.0)γ′

[a] Coupling too small to be measured.

TABLE 4

Approximate shielding effects of Ph_2PO and PhS in ^{13}C n.m.r. spectra

alkyl $X-\overset{\alpha}{C}-\overset{\beta}{C}-\overset{\gamma}{C}-\overset{\delta}{C}$

allyl $X-\overset{\alpha}{C}-\overset{\beta}{C}=\overset{\gamma}{C}-\overset{\delta}{C}$

vinyl $X-\overset{\alpha}{C}=\overset{\beta}{C}$

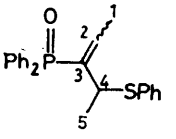
X	System	Chemical shift increment for carbon atoms (p.p.m.)[g]			
		α	β	γ	δ
Ph_2PO	alkyl	+18 [a]	−1	−1	0
	allyl	+16	*b*	+6	0
	vinyl	+8	+11	*b*	0
PhS	alkyl	+19	+10	−1	0
	allyl	+19	+5	−2	−2
	vinyl	*b*	*b*	*b*	*b*
			(+8) [c]	(−1) [c]	

[a] Falling to +10 if the chain is branched at this point. [b] Insufficient data. [c] Estimated from the spectrum of (35).

The expected chemical shifts for the product of PhS migration (37), calculated from Table 4, agree reasonably well with the observed values (Table 5). The product (35) from the rearrangement of the benzaldehyde adduct (33) has ^{13}C chemical shifts which could just fit either structure (35) or (40) but the ^{31}P-^{13}C coupling constants will fit only structure (35) (Table 6).

TABLE 5

^{13}C N.m.r. of the product of PhS migration (37)



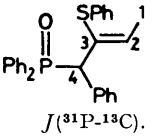
(37)

J_{CP} in parentheses		Observed	
C atom	Calc.	*E*-(37)	*Z*-(37)
1	24	21.4(3)	22.2(4.5)
2	141	144.2(3)	144.6(6.8)
3		*a*	*a*
4	46	42.8(14)	44.6(15)
5	24	16.0(10)	17.1(10)

[a] Signal concealed under those for the aromatic carbons.

TABLE 6

^{13}C N.m.r. spectrum of the product (35) of Ph_2PO migration

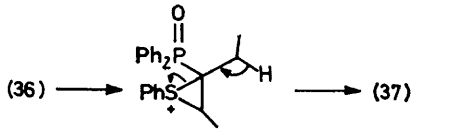


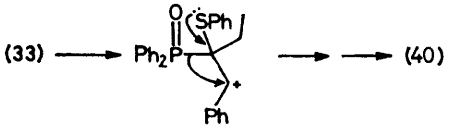
C atom	δ	$J(^{31}P$-$^{13}C)$.	Expected *J*
1	16.7	~0	v. small
2	136.9	6	5—10
3	*a*	*a*	0—5
4	53.9	61	60—90

[a] Signal concealed by signals of aryl carbon atoms.

Most significant is the large coupling observed for C-4 (60 Hz) typical of a carbon next to phosphorus but atypical [*cf.* values of 14 and 15 Hz for *E*- and *Z*-(37) respectively] for a carbon atom β to Ph_2PO. The shielding values under ' vinyl sulphide ' in Table 4 can then be estimated.

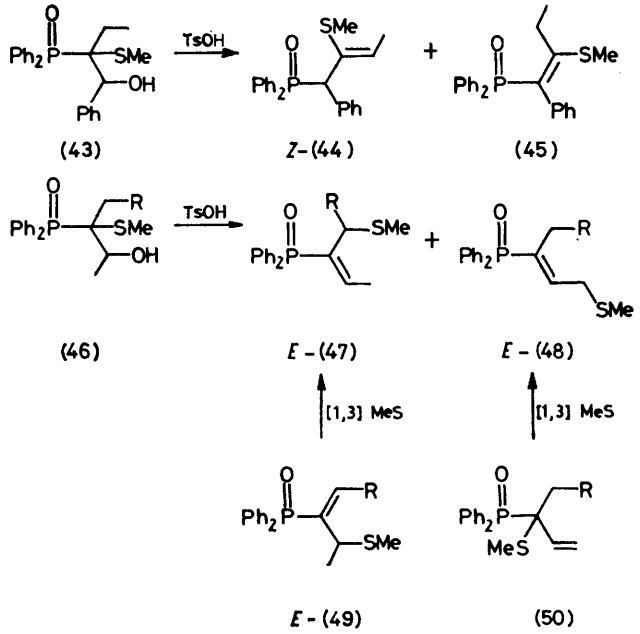
Ph_2PO vs. PhS *Migration*.—Ph_2PO thus migrates in the rearrangement of the benzaldehyde adduct (33) to give (35) while PhS migrates in the rearrangement of the acetaldehyde adduct (36) to give (37). This is reasonable





if participation by sulphur (41) is needed for (36) but not for (33) which can react *via* the secondary benzyl cation (42). The rearrangement of (36) is so far the only example in which Ph_2PO remains behind at the migration origin while another group migrates, and it presumably does so because no positive charge need arise next to it during the reaction (41).

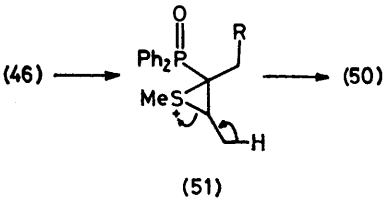
Rearrangement of the Methylthio-analogues (6; R^2 = Me).—The benzaldehyde adduct (43) also rearranged by



Ph_2PO migration but the products were the allyl (44) (26%) and vinyl (45) (51%) phosphine oxides in an equilibrium mixture.

The acetaldehyde adducts (46; R = H or Me) gave some products derived from MeS migration; (46; R = Me) gave the allyl sulphides (49; R = Me) as a minor product and (46; R = H) gave the product (47; R = H) of [1,2] followed by [1,3] [1] MeS shifts in 35% yield. However, both compounds lost water to give (50) which isomerised by a [1,3] MeS shift under the reaction conditions to compounds (48) which we have made by sulphenylation of allylphosphine oxides.[15] Thus (48; R = Me) was the major product from (46; R = Me); (48; R = H) was formed in 35% yield. The reactions thus follow the general pattern of the PhS compounds with the loss of water as an alternative to MeS or Ph_2PO migration.

Conclusions.—These rearrangements are unlikely to be of any use in synthesis as Ph_2PO migration is the major pathway only when the migration terminus is secondary and benzylic. The reactions are remarkable for the first appearance of elimination without rearrangement when either Ph_2PO or RS groups are at the migration origin, and for the first migration of any other group (RS in this case) when Ph_2PO is at the migration origin. This is presumably because Ph_2PO



hinders the migration of a group which cannot participate (*e.g.* alkyl) but does not hinder the participation of RS, that is the first step of RS migration. It does hinder the second step [*e.g.* (41)] so that the RS migrations, when they occur, are the slowest we have ever observed and direct elimination [*e.g.* (46) ⟶ (48)] can compete. This suggests that direct elimination also involves participation by sulphur (51).

EXPERIMENTAL

General procedures have been described before.[2,5]

2-Diphenylphosphinoyl-2-methoxy-1-phenylpropan-1-ol (11; R = Ph).—1-Methoxyethyldiphenylphosphine oxide [6] (1.25 g) in dry THF (30 ml) was stirred with lithium di-isopropylamide (LDA) [from di-isopropylamine (0.8 ml) and n-butyl-lithium (2.2 ml; 2.4M-solution in hexane)] in THF (6 ml) at 0 °C for 10 min. The solution was cooled to −78 °C and benzaldehyde (0.5 ml) in dry THF was added dropwise to discharge the red colour. The solution was allowed to warm to room temperature and then saturated ammonium chloride solution (30 ml) and ether (30 ml) were added. The aqueous layer was extracted with ether (3 × 30 ml) and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (ethyl acetate) gave the HR_F isomer of the *alcohol* (11; R = Ph) (860 mg, 49%) as needles, m.p. 177—179 °C, R_F (EtOAc) 0.45; τ($CDCl_3$) 1.6—2.8 (15 H, m, Ph_2PO and Ph), 4.95 (1 H, s, OH), 4.97 (1 H, d, J_{PH} 9 Hz, C*H*OH), 7.32 (3 H, s, OMe), 8.58 (3 H, d, J_{PH} 16 Hz, PCMe); *m/e* 348 ($M - H_2O$, 7%),

260 (96), 245 (100), and 201 (Ph_2PO^+, 29) (Found: $M - H_2O$, 348.125 8. $C_{22}H_{21}O_2P$ requires $M - H_2O$, 348.127 9) and the LR_F isomer of the *alcohol* (680 mg, 39%), m.p. 171—173 °C, R_F (EtOAc) 0.35; τ($CDCl_3$) 1.9—3.0 (15 H, m, Ph_2PO and Ph), 4.96 (1 H, d, J_{PH} 13 Hz, C*H*OH), 5.42 (1 H, s, OH), 6.64 (3 H, s, OMe), 8.56 (3 H, d, J_{PH} 15 Hz, PCMe); *m/e* 348 ($M - H_2O$, 64%), 260 (97), and 245 and 201 (Ph_2PO^+, 54) (Found: C, 72.0; H, 6.3; P, 8.4. $C_{22}H_{23}O_3P$ requires C, 72.1; H, 6.3; P, 8.5%).

3-*Diphenylphosphinoyl*-3-*methoxybutan*-2-*ol* (11; R = Me).—In a similar way 1-methoxyethyldiphenylphosphine oxide (1.25 g), LDA [from n-butyl-lithium (2.1 ml; 2.4M-solution in hexane) and di-isopropylamine (0.75 ml) in THF] and acetaldehyde (0.3 ml) in THF gave a gum which, after column chromatography (EtOAc), gave the *alcohol* (11; R = Me) (888 mg, 61%) as a gummy mixture of diastereoisomers, R_F (EtOAc) 0.25; τ($CDCl_3$) 1.7—2.8 (10 H, m, Ph_2PO), 5.80 and 5.96 (1 H, q, *J* 6 and q, *J* 7 Hz, C*H*Me), 6.0—6.5 (1 H, broad s, OH), 6.74 (3 H, s, OMe), 8.53 and 8.56 (3 H, d, J_{PH} 15 and d, J_{PH} 16 Hz, PCMe), 8.84 and 8.86 (3 H, d, *J* 7 and d, *J* 6 Hz, CH*Me*); *m/e* 305 (M + H, 8%), 286 ($M - H_2O$, 96), 271 (79), 260 (81), 245 (93), and 201 (Ph_2PO^+, 100) (Found: M + H, 305.130 3. $C_{17}H_{22}O_3P$ requires M + H, 305.130 6).

2-*Diphenylphosphinoyl*-2-*methoxy*-4-*methylpentan*-3-*ol* (11; R = Pr^i).—Similarly, 1-methoxyethyldiphenylphosphine oxide (1.25 g), LDA [from n-butyl-lithium (22 ml of a 2.4M in hexane) and di-isopropylamine (0.8 ml) in THF] and isobutyraldehyde (0.5 ml) in THF gave a gum which, after column chromatography (EtOAc), gave the HR_F isomer of the *alcohol* (11; R = Pr^i) (621 mg, 39%), m.p. 146—147 °C, R_F (EtOAc) 0.45; τ($CDCl_3$) 1.6—2.7 (10 H, m, Ph_2PO), 6.23 (1 H, s, OH), 6.32 (1 H, dd, J_{PH} 16, J_{HH} 5.5 Hz, C*H*OH), 6.65 (3 H, s, OMe), 7.7—8.2 (1 H, m, CHC*H*Me_2), 8.44 (3 H, d, J_{PH} 15 Hz, PCMe), 9.023 (3 H, d, *J* 6.5 Hz, CH*Me*$_2$*), and 9.21 (3 H, d, *J* 6.5 Hz, CH*Me*$_2$*); *m/e* 333 (M + H, 1%), 314 ($M - H_2O$, 7), 299 (97), 289 (48), 260 (64), 245 (71), and 201 (Ph_2PO^+, 100) (Found: C, 68.7; H, 7.4; P, 9.5. $C_{19}H_{25}O_3P$ requires C, 68.7; H, 7.6; P, 9.3%) and the LR_F isomer of the *alcohol* (607 mg, 38%), m.p. 129—130 °C, R_F (EtOAc) 0.3; τ($CDCl_3$) 1.6—2.7 (10 H, m, Ph_2PO), 5.71 (1 H, s, OH), 6.17 (1 H, dd, J_{PH} 10, J_{HH} 4 Hz, C*H*OH), 6.74 (3 H, s, OMe), 7.7—8.2 (1 H, m, C*H*Me_2), 8.40 (3 H, d, J_{PH} 16 Hz, PCMe), 8.97 (3 H, d, *J* 6 Hz CH*Me*$_2$*), 9.00 (3 H, d, *J* 7 Hz, CH*Me*$_2$*); *m/e* 314 ($M - H_2O$, 3%), 299 (33), 260 (28), 245 (44), 202 (Ph_2POH^+, 100), and 201 (Ph_2PO^+, 72) (Found: C, 68.6; H, 7.7; P, 9.5. $C_{19}H_{25}O_3P$ requires C, 68.7; H, 7.6; P, 9.3%).

1-*Diphenylphosphinoyl*-1-*phenylpropan*-2-*one* (16).—The alcohol (11; R = Ph) (150 mg), in solution in TFA (0.4 ml), was kept at 30 °C in an n.m.r. tube for 2.5 h. The mixture was poured into sodium hydrogen carbonate solution (30 ml), extracted with chloroform (3 × 30 ml), and the organic layers dried ($MgSO_4$) and evaporated under reduced pressure to give fine needles of the *ketone* (16) (140 mg, 93%), sublimes 235—239 °C, R_F (EtOAc) 0.4; $\nu_{max.}$ (Nujol mull) 1 708 (C=O) and 1 108 cm^{-1} (P=O); τ($CDCl_3$) 1.9—3.0 (15 H, m, Ph_2PO and Ph), 5.21 (1 H, d, J_{PH} 10 Hz, PCH), 7.72 (3 H, s, COMe); *m/e* 334 (M^+, 13%), 319 (4), 292 (45), 219 [$Ph_2P(OH)_2^+$, 100], and 201 (Ph_2PO^+, 47) (Found: M^+, 334.110 7. $C_{21}H_{19}O_2P$ requires M, 334.112 1).

2-*Diphenylphosphinoyl*-2-*methoxy*-1-*methylpropyl Toluene*-p-*sulphonate* (17).—The alcohol (11; R = Me) (733 mg) was dissolved in dry THF (70 ml) and n-butyl-lithium (2 ml; 1.5M-solution in hexane) was added at 0 °C. A solution of toluene-*p*-sulphonyl chloride (800 mg) in dry THF (10 ml) was added and the mixture stirred for 30 min. Saturated sodium hydrogen carbonate solution (50 ml) was added, the organic layer separated, washed with dilute hydrochloric acid (50 ml), and brine (50 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography (EtOAc) gave the *tosylate* as a mixture of diastereoisomers (888 mg, 80%), R_F (EtOAc) 0.45; τ($CDCl_3$) 1.7—2.9 (14 H, m, Ph_2PO and OSO_2Ar), 4.84 and 5.17 (1 H, dq, J_{PH} 9, J_{HH} 7, and dq, J_{PH} 7, J_{HH} 6 Hz, C*H*Me), 6.63 and 7.08 (3 H, two s, OMe), 7.54 and 7.59 (3 H, two s, ArMe), 8.50 and 8.69 (3 H, d, J_{PH} 15 and d, J_{PH} 14 Hz, PCMe), and 8.61 and 8.84 (3 H, d, *J* 6 and d, *J* 7 Hz, CH*Me*); *m/e* 286 (M − TsOH, 30%), 271 (46) and 201 (Ph_2PO^+, 100) (Found: M − TsOH, 286.112 3. $C_{17}H_{19}O_2P$ requires M − TsOH, 286.112 3).

2-*Diphenylphosphinoyl*-1-*isopropyl*-2-*methoxypropyl Toluene*-p-*sulphonate* (19).—In the same way, the HR_F isomer of the alcohol (11; R = Pr^i) (400 mg), n-butyl-lithium (1 ml; 1.5M solution in hexane), and toluene-*p*-sulphonyl chloride in THF gave a gummy crystalline solid. Recrystallisation from ethyl acetate gave the *tosylate* (310 mg, 53%) as fine hexagonal plates, m.p. 137—139 °C, R_F (EtOAc) 0.50; τ($CDCl_3$) 1.6—2.7 (10 H, m, Ph_2PO), 2.25 and 2.72 (4 H, ABq, J_{AB} 8 Hz, OSO_2Ar), 5.19 (1 H, d, *J* 5 Hz, C*H*OTs), 7.33 (3 H, s, OMe), 7.2—7.7 (1 H, m, C*H*Me_2), 7.57 (3 H, s, ArMe), 8.43 (3 H, d, J_{PH} 14 Hz, PCMe), 9.14 (3 H, d, *J* 7 Hz, CHMe_2*), 9.50 (3 H, d, *J* 7 Hz CHMe_2*); *m/e* 314 (M − TsOH, 21%), 299 (64), 271 (48), and 201 (Ph_2PO^+, 100) (Found: C, 64.2; H, 6.4; P, 6.6. $C_{26}H_{31}O_5P$ requires C, 64.2; H, 6.4; P, 6.4%).

Solvolysis of the Tosylate (17).—The tosylate (17) (100 mg) was stirred in acetic acid (10 ml; dried by distillation from acetic anhydride–chromium trioxide) with sodium acetate (100 mg) at 70 °C for 1 day. The mixture was poured into water (50 ml), extracted with ether (3 × 50 ml), the organic layers washed with sodium hydrogen carbonate solution (2 × 50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give 3-*diphenylphosphinoylbutan*-2-*one* (18) (49 mg, 83%), m.p. 132—135 °C, R_F (EtOAc) 0.25; τ($CDCl_3$) 2.1—2.7 (10 H, m, Ph_2PO), 6.37 (1 H, dq, J_{PH} 13, J_{HH} 7 Hz, PC*H*Me), 7.82 (3 H, s, COMe), and 8.64 (3 H, dd, J_{PH} 16, J_{HH} 7 Hz, PCH*Me*); *m/e* 272 (M^+, 45%), 230 (32), 219 [$Ph_2P(OH)_2^+$, 55], and 201 (Ph_2PO, 100) (Found: C, 70.3; H, 6.4; P, 11.2. $C_{16}H_{17}O_2P$ requires C, 70.6; H, 6.3; P, 11.4%).

Solvolysis of the Tosylate (19).—Similarly, treatment of the tosylate (19) (100 mg) with dry acetic acid (10 ml) and sodium acetate (100 mg) gave a yellow crystalline solid which was separated by preparative t.l.c. (EtOAc) into 3-*diphenylphosphinoyl*-2-*methoxy*-4-*methylpent*-1-*ene* (20) (25 mg, 39%), sublimes 165—170 °C, R_F (EtOAc) 0.4; τ($CDCl_3$) 1.9—2.8 (10 H, m, Ph_2PO), 5.79 (1 H, t, *J* 3 Hz, C=C*H*$_2$), 6.10 (1 H, m, C=C*H*$_2$), 6.80 (3 H, s, OMe), 7.11 (1 H, t with fine splitting, *J* 9 and 2 Hz, PC*H*), 7.3—7.9 (1 H, m, C*H*Me_2), 8.95 (3 H, d, *J* 7 Hz, CHMe_2*), 9.08 (3 H, d, *J* 7 Hz, CHMe_2*); *m/e* 314 (M^+, 2%), 300 (9), 258 (62), 243 (76), 219 (64), and 201 (Ph_2PO^+, 100), and 3-*diphenylphosphinoyl*-4-*methylpentan*-2-*one* (21) (16 mg, 26%), sublimes 187—190 °C, R_F (EtOAc) 0.33; $\nu_{max.}$ ($CHCl_3$) 1 700 (C=O), 1 440 (P–Ph), 1 180 cm^{-1} (P=O); τ($CDCl_3$) 1.9—2.7 (10 H, m, Ph_2PO), 6.59 (1 H, t, $J_{PH} = J_{HH}$ 9 Hz, PCH), 7.1—7.6 (1 H, m, C*H*Me_2), 8.03 (3 H, s, COMe), 8.99 (3 H, d, *J* 7 Hz, CHMe_2*), and 9.06 (3 H, d, *J* 7 Hz, CHMe_2*); *m/e* 300 (M^+, 6%), 258 (50), 243 (81), 219 (33), and 201 (Ph_2PO^+,

100) (Found: C, 71.8; H, 7.1; P, 10.2. $C_{18}H_{21}O_2P$ requires C, 72.0; H, 7.1; P, 10.3%).

Hydrolysis of the Vinyl Ether (20).—The vinyl ether (20) (25 mg) was stirred in THF (10 ml) with concentrated hydrochloric acid (5 drops) and water (2 drops) at room temperature for 20 min. The mixture was poured into ether (50 ml) washed with sodium hydrogen carbonate solution (15 ml) and brine (15 ml), and then dried ($MgSO_4$) and evaporated to give the above ketone (21) (24 mg, 100%).

3-*Diphenylphosphinoyl*-3-*methylthiobutan*-2-*ol* (46; R = H).—(1-Methylthioethyl)diphenylphosphine oxide [5] (1 g, 5.6 mmol) was treated with butyl-lithium (2.2 ml, 1.8M in hexane) in THF (30 ml) saturated with anhydrous lithium bromide at −78°. After 0.2 h, acetaldehyde (0.22 ml, 4 mmol) was added and after 2 min at −78 °C, ammonium chloride solution was added to the almost colourless solution and it was allowed to warm to room temperature. The product was extracted with chloroform (3 × 30 ml), the chloroform washed with dilute HCl (20 ml) and saturated brine (20 ml), and dried ($MgSO_4$), and evaporated to give a yellow gum. Chromatography (ethyl acetate) gave the HR_F isomer (*SR*, *RS*) of the *alcohol* (370 mg, 32%), m.p. 129—131 °C (from ethyl acetate–light petroleum), R_F (EtOAc) 0.34; $\nu_{max.}$ ($CHCl_3$) 3 300 (OH), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O); τ($CDCl_3$) 1.6—2.0, 2.4—2.6 (10 H, m, Ph_2), 4.3 (1 H, m, OH), 5.64 (1 H, dq, J_{HP} 6 Hz, J_{HH} 7 Hz, MeC*H*CP), 8.36 (3 H, s, MeS), 8.59 (3 H, d, J_{PH} 17 Hz, *Me*CP), and 8.64 (3 H, d, *J* 7 Hz, MeCH); *m/e* 302 ($M^+ - H_2O$, 3), 276 (*M* − MeCHO, 88), 261 (*M* − MeCHO − Me, 100), and 202 (Ph_2POH, 43%) (Found: C, 63.9; H, 6.9; P, 9.5. $C_{17}H_{21}O_2PS$ requires C, 63.7; H, 6.6; P, 9.7%), a mixture of isomers as a single fraction (233 mg, 20%), and the LR_F isomer (*SS*, *RR*) of the *alcohol* (133 mg, 11%), m.p. 134—136 °C (from ethyl acetate–light petroleum), R_F (EtOAc) 0.23; $\nu_{max.}$ ($CHCl_3$) 3 340 (OH), 1 440 (P–Ph), and 1 170 cm^{-1} (P=O); τ($CDCl_3$) 1.7—2.1, 2.4—2.6 (10 H, m, Ph_2P), 5.6—5.8 (1 H, broad s, OH), 5.83 (1 H, dq, J_{HP} 6, J_{HH} 7 Hz, MeC*H*OP), 8.10 (3 H, s, MeS), 8.62 (3 H, d, *J* 16 Hz, *Me*CP), and 8.70 (3 H, d, *J* 7 Hz, *Me*CH); *m/e* 302 ($M^+ - H_2O$, 4%), 276 (*M* − CH_3CHO, 58%), 261 (68), 202 (Ph_2POH, 43), and 151 (100) (Found: C,6 3.9; H, 6.7; P, 9.75. $C_{17}H_{21}O_2PS$ requires C, 63.7; H, 6.6; P, 9.7%).

3-*Diphenylphosphinoyl*-3-*methylthiopentan*-2-*ol* (46; R = Me).—(1-Methylthiopropyl)diphenyl phosphine oxide [5] (1.5 g, 5.2 mmol), was treated with n-butyl-lithium (3.2 ml; 1.8M in hexane) in THF (30 ml) saturated with anhydrous lithium bromide at −78 °C. After 0.2 h, quenching with acetaldehyde and immediate work up as before, gave a gummy solid. Column chromatography (ethyl acetate) gave the HR_F isomer (*SR*, *RS*) of the *alcohol* (946 mg, 55%), m.p. 118—120 °C, R_F (EtOAc) 0.44; $\nu_{max.}$ ($CHCl_3$) 3 300 (OH), 1 435 (PPh), and 1 175 (P=O) cm^{-1}; τ($CDCl_3$) 1.9—2.1, 2.4—2.6 (10 H, m, Ph_2P), 4.8 (1 H, broad s, OH), 5.60 (1 H, dq, J_{HP} 8 Hz, J_{HH} 6 Hz, MeC*H*OH), 7.6—8.3 (2 H, m, CH_2*Me), 8.59 (3 H, s, MeS), 8.67 (3 H, d. *J* 6 Hz, *Me*CH), and 8.87 (3 H, t, *Me*CH_2, *J* 7 Hz); *m/e* 316 (*M* − H_2O, 5%) 290 (*M* − MeCHO, 95), 202 (Ph_2POH, 65), and 185 (62) (Found: C, 64.7; H, 6.9; P, 9.6. $C_{18}H_{23}O_2PS$ requires C, 64.7; H, 6.9; P, 9.3%), and the LR_F isomer (*SS*, *RR*) of the *alcohol* (409 mg, 24%), m.p. 162—164 °C, R_F (EtOAc) 0.28; $\nu_{max.}$ ($CHCl_3$) 3 300 (OH), 1 440 (P–Ph), and 1 160 cm^{-1} (P=O); τ($CDCl_3$) 1.6—2.0, 2.4—2.6 (m, 10 H, Ph_2P), 5.6 (1 H, broad s, OH), 5.57 (1 H, dq, J_{PH} 12 Hz, J_{HH} 6 Hz, MeC*H*OH), 7.6—8.0 (1 H, m, CH_2*Me), 8.14 (3 H, s, MeS), 8.2—8.6 (1 H, m, CH_2*Me), 8.75 (3 H, d, *J* 6 Hz, *Me*CH), and 9.04 (3 H, t, *J* 7 Hz, $MeCH_2$); *m/e* 335 (M^+, 1, 3%), 316 (*M* − H_2O, 10), 290 (*M* − MeCHO, 100), 275 (65), and 202 (Ph_2POH, 90) (Found: C, 64.8; H, 7.0; P, 9.0. $C_{18}H_{23}O_2PS$ requires C, 64.7; H, 6.9; P, 9.3%).

2-*Diphenylphosphinoyl*-2-*methylthio*-1-*phenylbutan*-1-*ol* (43).—(1-Methylthiopropyl)diphenylphosphine oxide [5] (1 g, 3.5 mmol) was treated with n-butyl-lithium (2.1 ml; 1.8M in hexane) in THF (40 ml) saturated with anhydrous lithium bromide at −78 °C. After 0.2 h, quenching with benzaldehyde and immediate work-up as before, gave a gummy solid. Recrystallisation from ethyl acetate–light petroleum gave the alcohol as a mixture of diastereoisomers (1.22 g, 90%). Column chromatography (ethyl acetate) gave a 4 : 1 mixture of the HR_F isomer (*SR*, *RS*) of the *alcohol*, m.p. 190—192 °C, R_F (EtOAc) 0.58; $\nu_{max.}$ ($CHCl_3$) 3 300 (OH), 1 440 (PPh), and 1 155 cm^{-1} (P=O); τ($CDCl_3$) 1.4—2.8 (15 H, m, Ph_2P and Ph), 4.24 (1 H, broad s, OH), 4.61 (1 H, d, *J* 8 Hz, PhC*H*CP), 7.4—8.6 (2 H, m, CH_2*Me), 8.76 (3 H, t, *Me*CH_2), *J* 7.5 Hz), and 8.88 (3 H, s, MeS); *m/e* 397 ($M^+ + 1$, 5%), 379 (9), 290 (*M* − PhCHO, 100), 275 (62), and 202 (Ph_2POH, 75) (Found: C, 69.7; H, 6.4; P, 7.8. $C_{23}H_{25}O_2PS$ requires C, 69.7; H, 6.4; P, 7.8%), and the LR_F isomer (*SS*, *RR*) of the *alcohol*, m.p. 151—153 °C, R_F 0.40 (EtOAc); $\nu_{max.}$ ($CHCl_3$) 3 300 (OH), 1 440 (P–Ph), and 1 155 cm^{-1} (P=O); τ($CDCl_3$) 1.7—2.8 (15 H, m, Ph_3), 4.5 (1 H, broad s, OH), 5.08 (1 H, d, *J* Hz, Ph-C*H*CHP), 7.7—8.5 (2 H, m, CH_2*Me) overlain by 8.23 (3 H, s, MeS), and 8.71 (3 H, t, *J* 7 Hz, *Me*CH_2); *m/e* 397 ($M^+ + 1$, 3%), 378 (*M* − H_2O, 7), 290 (84) 275 (*M* − PhCHO − Me, 100), and 202 (Ph_2POH, 72) (Found: C, 69.7; H, 6.55; P, 7.7. $C_{23}H_{25}O_2PS$ requires C, 69.7; H, 6.4; P, 7.8%).

Conversion of the Adduct (32) *into Vinyl Sulphides* E- *and* Z-(31).—(a) *The* (SR, RS) *isomer*. The HR_F (*SR*, *RS*) isomer of the above alcohol (32) (147 mg) in THF (10 ml) was added to sodium hydride (24 mg of a 50% suspension in oil) and washed with light petroleum (b.p. 30—40 °C). The reaction mixture was stirred at room temperature for 17 h, the thick white precipitate (Ph_2PO_2Na) removed on Celite, and the combined filtrate and CH_2Cl_2 washings evaporated to give, as a pale yellow oil, E-1-*phenyl*-2-*methylthiobut*-1-*ene* (69 mg) containing *ca.* 10% of the *Z*-isomer. It had R_F (CH_2Cl_2) 0.76; τ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 3.88 (1 H, s, C=CH), 7.52 (2 H, q, *J* 7 Hz, CH_2Me), 7.67 (3 H, s, SMe), and 8.78 (3 H, t, *J* 7 Hz, CH_2*Me*).

(b) *The* (SS, RR) *isomer*. In the same way the LR_F (*SS*, *RR*) isomer (60 mg) gave Z-1-*phenyl*-2-*methylthiobut*-1-*ene* (27 mg), R_F (CH_2Cl_2) 0.75; τ($CDCl_3$) 2.0—2.9 (5 H, m, Ph), 3.48 (s, 1 H, C=CH), 7.50 (2 H, q, *J* 8 Hz, CH_2Me), 7.74 (3 H, s, SMe), and 8.72 (3 H, t, *J* 8 Hz, CH_2*Me*).

1-*Phenyl*-2-*methylthiobut*-1-*ene by the One-step Horner–Wittig Procedure*.—1-(Methylthio)propyldiphenylphosphine oxide [5] (30) (0.5 g, 1.73 mmol) was treated with BuLi and benzaldehyde by the method described before [5] to give a pale yellow oil; column chromatography (silica, eluted with CH_2Cl_2) gave the *vinyl sulphide* (31) (278 mg, 90%), R_F (CH_2Cl_2) 0.75, $\nu_{max.}$ (film) 1 600, 1 580, and 1 510 cm^{-1} (Ph); the n.m.r. spectrum showed a 4 : 1 ratio of *E* : *Z* isomers (see above); *m/e* 178 (M^+, 100%) and 163 (*M* − Me, 20) (Found: M^+, 178.081 4. $C_{11}H_{14}S$ requires *M*, 178.081 6).

3-*Diphenylphosphinoyl*-3-*phenylthiopentan*-2-*ol* (36).—(1-Phenylthiopropyl)diphenylphosphine oxide [5] (1 g, 2.8 mmol) was treated with n-butyl-lithium (1.3 ml; 2.4M in

hexane) in THF (30 ml) saturated with anhydrous lithium bromide at −78 °C. After 0.2 h, quenching with acetaldehyde and immediate work-up as before gave a gummy solid. Recrystallisation from ethyl acetate–light petroleum gave the alcohol as a mixture of isomers (700 mg, 62%). Further recrystallisation gave the pure LR_F isomer (*SS*, *RR*) of the *alcohol*, m.p. 182—184 °C, R_F (EtOAc) 0.38; $\nu_{max.}$ ($CHCl_3$) 3 340 (OH), 1 480 (PhS), 1 440 (PPh), and 1 160 (P=O) cm^{-1}; τ($CDCl_3$) 1.6—1.8, 2.4—2.9 (15 H, Ph_2P and PhS), 5.35 (1 H, dq, J_{HP} 12 Hz, J_{HH} 6 Hz, PCC*H*Me), 5.6—6.3 (1 H, broad m, OH), 7.7—8.8 (2 H, m, MeCH_2*CP), 8.62 (3 H, d, *Me*CHOH, *J* 6 Hz), and 9.1 (3 H, t, J_{HH} 7.5 Hz, *Me*CH_2); *m/e* 378 ($M^+ - H_2O$, 2%), 352 (*M* − MeCHO, 65), 337 (22), and 202 (Ph_2POH, 100) (Found: C, 69.9; H, 6.6; P, 8.1. $C_{23}H_{25}O_2PS$ requires C, 69.7; H, 6.4; P, 7.8%).

2-*Diphenylphosphinoyl*-2-*phenylthio*-1-*phenylbutan*-1-*ol* (33).—(1-Phenylthiopropyl)diphenylphosphine oxide [5] (1 g, 2.8 mmol) was treated with n-butyl-lithium (1.3 ml; 2.4M in hexane) in THF (30 ml) at −78 °C. After 0.2 h, benzaldehyde (0.31 ml, 3.1 mmol) was added, and immediate work-up as before gave an oil. Crystallisation (ethyl acetate–petroleum) gave the alcohol (1 diastereoisomer) (469 mg, 36%), m.p. 164—165 °C, R_F 0.62 (EtOAc); $\nu_{max.}$ ($CHCl_3$) 3 300 (OH), 1 490 (PPh), and 1 150 (P=O) cm^{-1}; τ($CDCl_3$) 1.2—1.4 (2 H, m, *ortho*-phenyl H), 1.6—1.8 (2 H, m, *ortho*-phenyl H), 2.4—3.4 (14 H, m, *meta*- and *para*-phenyl H, another Ph, and *meta* and *para* protons of a further Ph), 3.56 (1 H, s, OH), 3.64 (2 H, m, *ortho*-phenyl H), 4.54 (1 H, d, *J* 8 Hz, PCC*H*OH), 8.0—8.9 (2 H, m, CH_2*Me), and 8.66 (3 H, t, *J* 4 Hz, *Me*CH_2); *m/e* 442 ($M^+ - H_2O$, 1%), 352 (*M* − PhCHO, 83), 279 (Ph_3POH, 100), 243 ($Ph_2POCHEt$, 63), 240 (90), and 202 (Ph_2POH, 73) (Found: C, 73.1; H, 6.0; P, 6.5. $C_{28}H_{27}O_2PS$ requires C, 73.3; H, 5.9; P, 6.75%).

Conversion of the Adduct (33) *into the Vinyl Sulphide.*—The crude product from the above synthesis of (33) (5 : 1 ratio of HR_F : LR_F diastereoisomers) (300 mg) in THF (25 ml) was added to sodium hydride (48 mg, suspension in oil washed with light petroleum, b.p. 30—40 °C) and stirred at room temperature for 17 h. The mixture was filtered through Celite, the precipitate washed with CH_2Cl_2, and the solvent evaporated from the filtrate to give 1-phenyl-2-phenylthiobut-1-ene (6; R = Me, R^2 = R^3 = Ph) (185 mg) identified by its n.m.r. spectrum [5] as a 5 : 1 ratio of *E* : *Z* isomers.

E-2-*Diphenylphosphinoyl*-1-*phenylbut*-1-*ene* (34).—2-Diphenylphosphinoyl-2-phenylthio-1-phenylbutan-1-ol (90 mg) was dissolved in TFA (0.3 ml) and the reaction followed by n.m.r. spectroscopy at 37 °C. The solution turned brown and cloudy and after 0.2 h the n.m.r. spectrum showed the reaction was complete. The reaction mixture was poured into water, neutralised with sodium carbonate solution, and the product extracted with chloroform (3 × 5 ml). The chloroform was dried ($MgSO_4$) and evaporated to give a yellow oil. Preparative t.l.c. gave the *vinyl phosphine oxide* (36 mg, 56%) as a gum, R_F (EtOAc) 0.25; $\nu_{max.}$ ($CHCl_3$) 1 440 (P–Ph) and 1 160 cm^{-1} (P=O); τ($CDCl_3$) 2.1—2.6 (10 H, m, Ph_2P), 2.64 (5 H, s, PhC), 2.93 (1 H, d, J_{HP} 22 Hz, *cis*-HC=CP), 7.37 (2 H, dq, J_{HP} 18 Hz, J_{HH} 8 Hz, CH_2CP), and 9.02 (3 H, t, *J* 8 Hz, *Me*CH_2); *m/e* 332 (M^+, 50%) and 202 (Ph_2POH, 100) (Found: M^+, 332.130 5. $C_{22}H_{21}OP$ requires *M*, 332.132 9).

1-*Diphenylphosphinoyl*-1-*phenyl*-2-*phenylthiobut*-2-*ene* (35).—2-Diphenylphosphinoyl-2-phenylthio-1-phenylbutan-1-ol (1.0 g, 2.2 mmol) and TsOH (460 mg, 2.4 mmol) were heated under reflux in toluene (35 ml) in a Dean-Stark apparatus for 0.3 h, and then poured into sodium hydrogen carbonate solution. The product was extracted into chloroform (3 × 30 ml), and the chloroform extract was dried ($MgSO_4$) and evaporated to give a pale yellow gum. Recrystallisation from ethyl acetate–light petroleum gave the rearranged *phosphine oxide* (490 mg, 51%), m.p. 176—177 °C, R_F (EtOAc) 0.59; $\nu_{max.}$ 1 600, 1 580, 1 490 (Ph), 1 440 (PPh), and 1 180 cm^{-1} (P=O); τ($CDCl_3$) 2.0—2.9 (21 H, m, Ph_2P, PhS, Ph, and vinyl H), 5.85 (1 H, d, *J* 9 Hz, PhC*H*CP), and 8.13 (3 H, dd, J_{HH} 6 Hz, J_{HP} 1 Hz, *Me*CH=CCP); *m/e* 440 (M^+, 27%), 331 (*M* − PhS, 100), 311 (32), 238 (*M* − Ph_2POH, 85), 202 (Ph_2POH, 100), 201 (Ph_2PO, 73), and 130 (70) (Found: C, 76.2; H, 5.7; P, 6.8. $C_{28}H_{25}OSP$ requires C, 76.3; H, 5.7; P, 7.0%).

2-*Phenylthio*-3-*diphenylphosphinoylpent*-3-*ene* (37).—Diphenylphosphinoyl-3-phenylthiopentan-2-ol (0.5 g, 1.25 mmol) and TsOH (265 mg, 1.4 mmol) were heated together under reflux in AnalaR toluene (35 ml) in a Dean-Stark apparatus for 17 h. The reaction mixture was poured into sodium hydrogen carbonate solution, and extracted with $CHCl_3$ (3 × 30 ml). The $CHCl_3$ extract was dried ($MgSO_4$) and evaporated to give a pale yellow oil. Preparative t.l.c. (ethyl acetate) gave the rearranged *vinyl phosphine oxide* (335 mg, 70%) as a mixture of geometric isomers, R_F (EtOAc) 0.29 and 0.35; $\nu_{max.}$ ($CHCl_3$) 1 630 (C=C), 1 600, 1 480 (PhS), 1 440 (PPh), and 1 170 (P=O) cm^{-1}; *m/e* 378 (M^+, 35%), 345 (23), 296 (*M* − PhS, 55), 202 (Ph_2POH, 85), 201 (Ph_2PO, 100), 110 (PhSH, 25), and 77 (58) (Found: M^+, 378.119 6. $C_{23}H_{23}OPS$ requires *M*, 378.120 6).

A small amount of the phosphine oxide was separated into its geometric isomers by preparative t.l.c. (two elutions, ethyl acetate) and the n.m.r. spectra were determined separately. HR_F = *E*-isomer, τ($CDCl_3$) 2.1—2.9 (15 H, m, 3 Ph), 3.75 (1 H, dq, J_{HP} 22 Hz, J_{HH} 7.5 Hz, PC=C*H*Me, *cis*), 5.88 (1 H, dq, J_{HP} 16 Hz, J_{HH} 7 Hz, MeC*H*CP), 7.94 (3 H, dd, J_{HH} 7 Hz, J_{HP} 3 Hz, *Me*CH=CP), and 8.52 (3 H, d, J_{HH} 7 Hz, *Me*CHSPh). LR_F = *Z*-isomer, τ($CDCl_3$) 2.0—3.0 (15 H, m, 3 Ph), 3.15 (1 H, dq, J_{HP} 37 Hz, J_{HH} 7.5 Hz, MeC*H*=CP *trans*), 6.20 (1 H, dq, J_{HP} 10 Hz, J_{HH} 7 Hz, PCC*H*Me), 8.20 (3 H, dd, J_{HH} 7.5 Hz, J_{HP} 3 Hz, *Me*CH=CP), and 8.64 (3 H, d, *J* 7 Hz, *Me*CHSPh).

Solvolysis of 2-*Diphenylphosphinoyl*-2-*methylthio*-1-*phenylbutan*-1-*ol.*—Diphenylphosphinoyl-2-methylthio-1-phenylbutanol (200 mg, 0.5 mmol) was heated with TsOH (96 mg, 0.5 mmol) in toluene under reflux in a Dean-Stark apparatus for 1 h. The reaction mixture was poured into sodium carbonate solution, and extracted with $CHCl_3$ (3 × 30 ml). The organic extracts were dried ($MgSO_4$) and evaporated to give a pale gummy solid. T.l.c. showed the presence of a little vinyl phosphine oxide and two isomers of rearranged product. The product was purified by t.l.c. to give the HR_F isomer, 1-diphenylphosphinoyl-2-methyl-1-phenylthiobut-2-ene (44) (50 mg, 26%) a white gummy solid, R_F (EtOAc) 0.53; $\nu_{max.}$ ($CHCl_3$) 1 600, 1 500 (Ph), 1 435 (PPh), and 1 165 cm^{-1} (P=O); τ($CDCl_3$) 1.9—2.8 (15 H, m, Ph_2P and Ph), 3.02 (1 H, dq, J_{HP} 3 Hz, J_{HH} 6 Hz, PCC=C*H*Me), 5.53 (1 H, d, J_{HP} 10 Hz, PhC*H*CP), 8.00 (3 H, s, MeS), and 8.14 (3 H, dd, J_{HP} 6 Hz, J_{HH} 2 Hz, *Me*CH=CCP); *m/e* 378 (M^+, 19%), 331 (*M* − MeS, 81), 201 (Ph_2PO, 100), 176 (*M* − Ph_2POH, 35) and 129 (76); (Found: C, 72.7; H, 6.1; P, 7.9. $C_{23}H_{23}OPS$ requires C, 73.0; H, 6.1; P, 8.2%) and the LR_F isomer, 1-*diphenyl-*

phosphinoyl-2-methylthio-1-phenylbut-1-ene (45) (98 mg, 51%) as a colourless gum, R_F (EtOAc) 0.30; $\nu_{max.}$ ($CHCl_3$) 1 600, 1 500 (Ph), 1 435 (PPh), and 1 170 cm^{-1} (P=O); τ($CDCl_3$) 2.0—3.1 (15 H, m, Ph_2P and Ph), 6.84, 7.50 (2 H, two dq, J_{PH} 2 Hz, J_{HH} 7 Hz, and J_{PH} 17 Hz, J_{HH} 7 Hz, CH_2C=CP, two geometric isomers), 7.73 (3 H, s, MeS), 8.80, and 8.94 (3 H, t, t, J_{HH} 7 Hz, $MeCH_2$); *m/e* 378 (M^+, 29%), 331 (M − MeS, 100), 201 (Ph_2PO, 60), and 155 (19) (Found: M^+, 378.120 5. $C_{23}H_{23}OPS$ requires M, 378.120 6).

Solvolysis of 3-*Diphenylphosphinoyl-3-methylthiobutan-2-ol* (46; R = H).—The alcohol (46; R = H) (100 mg, 0.31 mmol) was heated with TsOH (75 mg, 0.4 mmol) in toluene (30 ml) under reflux in a Dean-Stark apparatus for 2 h. The reaction mixture was worked up as above, and the resultant oil purified by preparative t.l.c. The major band, R_F (EtOAc) 0.18, was a colourless oil, (62 mg, 70%) identified by n.m.r. and mass spectra to be an equal mixture of 3-diphenylphosphinoyl-1-methylthiobut-2-ene (48; R = H) and 2-diphenylphosphinoyl-1-methylthiobut-2-ene (47; R = H), *m/e* 302 (M^+, 20%), 287 (M − Me, 33), 256 (M − CH_2S, 100), 201 (Ph_2PO, 70), and 77 (90); τ($CDCl_3$) 2.2—2.7 (10 H, m, Ph_2), 3.4—3.9 (1 H, m, vinyl H), 6.56 [2 H, of one isomer, d, J_{HP} 14 Hz, S-CH_2-CP of (47; R = H)], 6.74 [2 H, of other isomer, dd, J_{HH} 8 Hz, J_{HP} 2 Hz, SCH_2-CHCP of (48, R = H)], 7.96 [3 H of one isomer, s, MeS of (48; R = H)], 8.06 [3 H, of other isomer, s, MeS of (47; R = H)], and 8.0—8.25 (complex mixture of doublets from both Me-C=C, 3 H). When the reaction was carried out in benzene under reflux (6 h), the same mixture of products was obtained but in 37% yield.

Solvolysis of 3-*Diphenylphosphinoyl-3-methylthiopentan-2-ol* (46; R = Me).—The alcohol (46; R = Me) (250 mg, 0.75 mmol) was heated with TsOH (170 mg, 0.9 mmol) under reflux in toluene (40 ml) in a Dean-Stark apparatus for 2 h. The reaction mixture was worked up as above, and the resultant oil purified by preparative t.l.c. The main band [R_F 0.28 (EtOAc)] gave a colourless gum (140 mg, 60%), tentatively assigned from its spectra to a mixture of (48; R = Me) (>50% of the product) and (49; R = Me). The presence of a small signal in the n.m.r. spectrum in the *exo*-methylene region (5.1 p.p.m.) may suggest the presence of a small amount of the intermediate (50; R = Me); *m/e* 316 (M^+, 12%), 301 (M − Me, 22), 269 (M − MeS, 100), 201 (Ph_2PO, 64), and 77 (37); τ($CDCl_3$. 2.1—2.6 (10 H, m, Ph_2P), 3.88 [<1 H, dt, J_{HP} 20 Hz, J_{HH} 7.5 Hz, PC=C*H*CH_2S in (48) (*E*-isomer), overlain by complex vinyl multiplet from MeC*H*=CP in (49)], 6.70 [<2 H, dd, J_{HH} 7.5 Hz, J_{HP} 3 Hz, PC=CCH_2SMe, in (48)], 7.4—8.0 [<2 H, m, MeCH_2CP in (48)], 7.92 [<3 H, s, MeS in (48)], 7.96, 8.02 (two small s, from other isomers), 8.15 [<3 H, dd, J_{HH} 12 Hz, J_{HP} 3 Hz, *Me*CH=CP in (49)], 8.55 [<3 H, d, J_{HH} 7 Hz, *Me*CHS in (49)], and 9.07 [<3 H, t, J_{HH} 7 Hz, *Me*CH_2 in (48)].

One-step Horner–Wittig Synthesis of 2-Methylthiostyrene (29).—Methylthiomethyldiphenylphosphine oxide [5] (28) (0.5 g, 1.9 mmol) in THF (30 ml) at −78 °C was treated with BuLi (1.2 ml, 2.1 mmol; 1.8M in hexane). The red solution was stirred at −78 °C for 15 min, benzaldehyde (0.21 ml, 2.1 mmol) was added, and the solution allowed to reach room temperature. Work-up as before [5] gave the vinyl sulphide identified by its n.m.r. spectrum [13] as a 20 : 1 *E* : *Z* mixture. Pure *E*-(29) was isolated by column chromatography (silica eluted with CH_2Cl_2).

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