Acyl Anion Equivalents: Synthesis of Ketones and Enones from α-Phenylthioalkylphosphine Oxides [1]

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The sulphenylated phosphine oxides $Ph_2P(O)\cdot CH(SR^2)R^1$, easily prepared from triphenylphosphine, diphenyl or dimethyl disulphide, and an alkyl halide, form anions which act as acyl anion equivalents. Reaction with aldehydes and ketones gives vinyl sulphides, which can be hydrolysed to carbonyl compounds. Reaction with α-phenylthio- and α-methoxy-aldehydes and ketones gives enone precursors. The scope and limitations of the method are described.

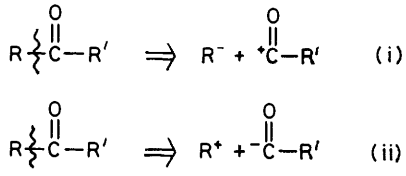
CONVENTIONAL ketone syntheses involve the addition of a carbon nucleophile (Grignard reagent, enolate anion, *etc.*) to a carbon electrophile (usually an acyl derivative), the electrophilic carbon atom becoming the new carbonyl carbon.[2] Equation (i) shows the disconnection corresponding to this approach. Recently a new family of ketone syntheses has been evolved using the same disconnection but with umpolung [3] [equation (ii)] so that the new carbonyl carbon atom is derived from the

[1] Preliminary communication, P. Blatcher, J. I. Grayson, and S. Warren, *J.C.S. Chem. Comm.*, 1976, 547.

[2] D. P. N. Satchell, R. S. Satchell, M. Cais, and A. Mandelbaum in 'The Chemistry of the Carbonyl Group,' ed. S. Patai, Wiley, London, 1966, pp. 233—330.

[3] D. Seebach and M. Kolb, *Chem. and Ind.*, 1974, 687.

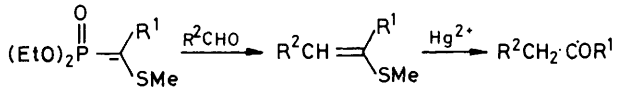
nucleophilic carbon of an acyl anion equivalent.[4] In the best known of these, the anion is stabilised by two



sulphur atoms, as in dithians [5] (1), and bis(phenylthio)-methane [1,6] (2). Others in this class contain one phosphorus and one sulphur atom [7] [*e.g.* (3)] and react with carbonyl compounds by the Wittig reaction to give vinyl sulphides (4) which can be hydrolysed to ketones (5).

These differ from the dithian routes in that a 1,2-alkylative carbonyl transposition [8] is involved, the final carbonyl carbon atom coming from what was originally an sp^3 carbon atom, and the carbonyl carbon atom of

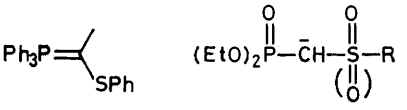
(1) (2)



(3) (4) (5)

the electrophile (R^2CHO) becoming a saturated carbon in the product. Green [9] originally used the anion from diethyl methylthiomethylphosphonate (3; $R^1 = H$) as an acyl anion equivalent, and this method was developed by Corey and Shulman [7] and others.[10,11] Modifications using phosphonium salts [12–15] (6) and phosphonate esters substituted with methyl- and phenyl-sulphinyl,[16,17] and phenylsulphonyl [17–19] (7) groups have been used in attempts to solve the three main problems of the method: (i) lack of a good general synthesis of the sulphur-containing Wittig reagents [the reagents (3) have to be obtained from (3; $R^1 = H$) [7]]; (ii) poor yields in the Wittig reaction, particularly with ketones; [7,9,10] and (iii) difficulties in converting the vinyl sulphides into carbonyl compounds.[20]

For most applications in synthesis, the diphenylphosphinoyl (Ph_2PO) group is superior to the triphenylphosphonium (Ph_3P^+) and the dialkoxyphosphinoyl [$(RO)_2PO$] groups in that the reagents are usually crystalline, reactivity and yields are higher, and separation of the Wittig reaction by-product, diphenylphosphinic acid, is very simple. We have therefore developed methods for ketone and enone synthesis using the Ph_2PO group in combination with the PhS or MeS



(6) (7)

groups * which have to a certain extent solved the three problems above. Our interest in these compounds arose from our work on Ph_2PO [21] and PhS [22] rearrangements, since either group might rearrange from the intermediate (15).[23]

Preparation of the Horner–Wittig Acyl Anion Equivalents.—Primary alkyldiphenylphosphine oxides (8) are readily available from triphenylphosphine *via* alkylation and hydrolysis [21,24] (Scheme 1). The anions from these compounds, formed with n-butyl-lithium in the presence of tetramethylethylenediamine (TMEDA), react readily with dimethyl or diphenyl disulphide to give the sulphenylated phosphine oxides (9) in high yield (Table 1)

TABLE 1

Synthesis of Horner–Wittig acyl anion equivalents (9) and (10)

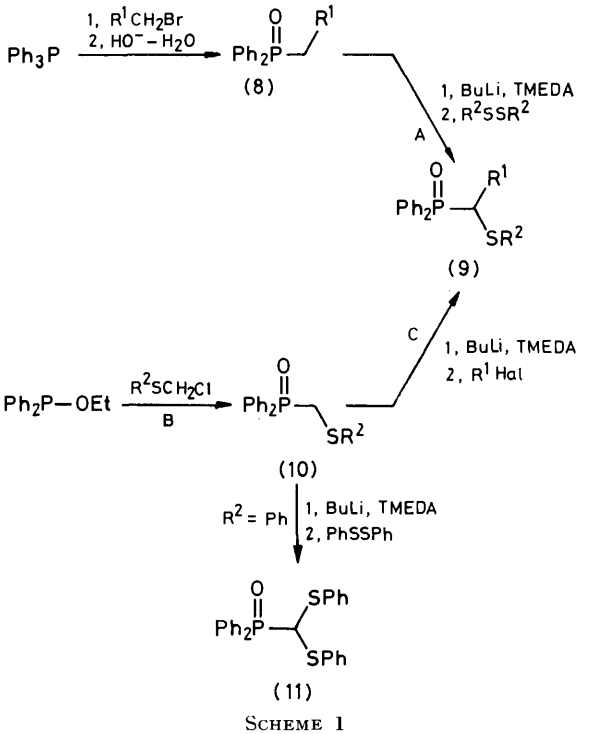
Method	R^1	Yield (%) R^2 = Ph	Yield (%) R^2 = Me
B	H	96	86
C	Me	69	75
A	Et	73	62
A	Pr^i	81	78
A	$PhCH_2$	79	
C	$PhCH_2$	84	
A	PhS	75	

* We have also developed ketone syntheses from methoxyalkyldiphenylphosphine oxides *via* enol ethers: C. Earnshaw, C. J. Wallis and S. Warren, *J.C.S. Chem. Comm.*, 1977, 314.

[4] O. W. Lever, *Tetrahedron*, 1976, **32**, 1943; B.-T. Gröbel and D. Seebach, *Synthesis*, 1977, 357.
[5] D. Seebach, *Synthesis*, 1969, 17; D. Seebach and E. J. Corey, *J. Org. Chem.*, 1975, **40**, 231.
[6] E. J. Corey and D. Seebach, *J. Org. Chem.*, 1966, **31**, 4097.
[7] E. J. Corey and J. I. Shulman, *J. Org. Chem.*, 1970, **35**, 777.
[8] B. M. Trost, K. Hiroi, and S. Kurozumi, *J. Amer. Chem. Soc.*, 1975, **97**, 438; B. M. Trost and K. Hiroi, *ibid.*, p. 6911.
[9] M. Green, *J. Chem. Soc.*, 1963, 1324.
[10] I. Shahak and J. Almog, *Synthesis*, 1969, 170; 1970, 145.
[11] H. M. McGuire, H. C. Odon, and A. R. Pinder, *J.C.S. Perkin I*, 1974, 1879.
[12] T. Mukaiyama, S. Fukuyama, and T. Kumamoto, *Tetrahedron Letters*, 1968, 3787.
[13] I. Vlattas and A. O. Lee, *Tetrahedron Letters*, 1974, 4451.
[14] G. Wittig and M. Schlosser, *Chem. Ber.*, 1961, **94**, 1373.
[15] H. J. Bestmann and J. Angerer, *Annalen*, 1974, 2085.
[16] M. Mikołajczyk, S. Grzejszczak, and A. Zatorski, *J. Org. Chem.*, 1975, **40**, 1979.
[17] M. Mikołajczyk, S. Grzejszczak, W. Midura, and A. Zatorski, *Synthesis*, 1975, 278.
[18] I. C. Popoff, J. L. Dever, and G. R. Leader, *J. Org. Chem.*, 1969, **34**, 1128.
[19] G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, 1972, **37**, 3547.
[20] A. J. Mura, G. Majetich, P. A. Grieco, and T. Cohen, *Tetrahedron Letters*, 1975, 4437.
[21] A. H. Davidson, C. Earnshaw, J. I. Grayson, and S. Warren, *J.C.S. Perkin I*, 1977, 1452.
[22] P. Brownbridge and S. Warren, *J.C.S. Perkin I*, 1977, 1131.
[23] J. I. Grayson and S. Warren, submitted to *J.C.S. Perkin I*.
[24] L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, 1958, **91**, 64; K. Sasse in Houben–Weyl, 'Methoden der Organischen Chemie,' Thieme, Stuttgart, 1963, vol. 12/1, pp. 144–150.

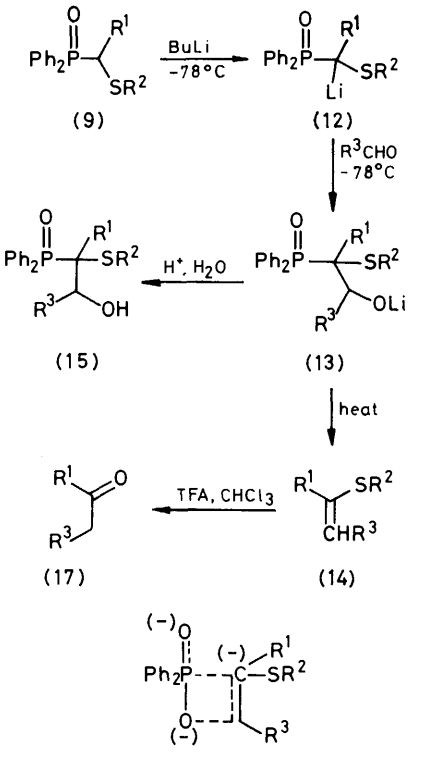
(absence of TMEDA leads to considerably lower yields). This route gives poor yields for $R^1 = H$, as the initial product (10; $R^2 = Ph$) is further sulphenylated under the reaction conditions to give a mixture of (10; $R^2 = Ph$) and the bis(phenylthio)-compound (11). Pure (11) can be obtained by sulphenylation of (10; $R^2 = Ph$) prepared by route B. The unsubstituted compounds (10) are made in high yield by the Arbusov reaction (route B in Scheme 1), and can themselves be converted into substituted compounds [*e.g.* (9; $R^1 = Me$)] by alkylation (again using BuLi and TMEDA to make the anions—route C, Scheme 1). Previous syntheses of sulphenylated phosphine oxides have produced only the unsubstituted compounds (10) and use the less readily available starting materials Ph_2PH [25] or Ph_2PLi.[26] All of the reagents (9) are stable crystalline compounds which can be purified and stored without special precautions.

Reactions of the Horner–Wittig Acyl Anion Equivalents (9) *with Aldehydes* (*Scheme* 2).—The sulphur atom on the α-position increases the stability of the anion (12) so that the first stage of the Horner–Wittig reaction to give the adduct (13) is slower. By contrast the second stage, (13) ⟶ (14), is faster, since the transition state (16)



SCHEME 1

has a partial negative charge on the α-carbon, enhancing the rate of P–C bond cleavage. Horner–Wittig reactions using the Ph_2PO group normally give adducts analogous to (15).[21] These can be isolated at room temperature without completion of the Wittig reaction to the olefin, which generally requires a sodium or potassium base. However, with a sulphur atom present,



SCHEME 2

warming the reaction mixture to room temperature for 0.5 h is enough to cause completion of the Wittig reaction (13) ⟶ (14) * (Table 2). The adducts (15) may be isolated by quenching with aqueous ammonium chloride immediately after the addition of the aldehyde at −78 °C.[23]

TABLE 2

Synthesis of vinyl sulphides from phosphine oxides (9) and aldehydes

	R^1	R^2	R^3	Yield (%) of vinyl sulphide (14)	Yield (%) of ketone (17)
1.	Et	Ph	Ph	93	78
2.	$PhCH_2$	Ph	n-Hexyl	93	93
3.	$PhCH_2$	Ph	Ph	90	97
4.	Pr^i	Ph	p-MeO·C_6H_4	94	86
5.	Pr^i	Ph	PhCH:CH	93	*a*
6.	H	Ph	3,4-$(CH_2O_2)C_6H_3$	92	*a*

[a] Could not be hydrolysed by conventional methods; see text.

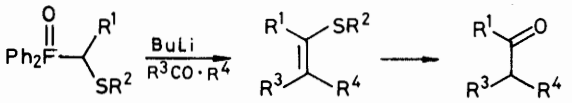
Reactions of the Horner–Wittig Acyl Anion Equivalents

* Similar results have been observed with other phosphine oxides: B. Lythgoe, T. A. Moran, M. E. N. Nambudiry, and S. Ruston, *J.C.S. Perkin I*, 1976, 2386; M. Schlosser and H. B. Tuong, *Chimia* (*Switz.*), 1976, **30**, 197.

[25] H. Hellmann and J. Bader, *Tetrahedron Letters*, 1961, 724.
[26] A. M. Aguiar, K. C. Hansen, and J. T. Mague, *J. Org. Chem.*, 1967, **32**, 2383.

(9) *with Ketones.*—One of the problems with phosphorus-containing acyl anion equivalents is their lack of reactivity in the Wittig reaction with ketones. Presumably the extra stability given to the anion (12) by the sulphur atom allows the sterically favourable abstraction of an α-proton to be the major reaction. Our alkylated reagents (9; R^2 = Ph) did not give Horner–Wittig products with ketones: for example the phosphine oxide (9; R^1 = Et, R^2 = Ph) was unchanged when treated with cyclohexanone or acetophenone using sodium or lithium bases.

The unsubstituted PhS reagents (9; R^1 = H, R^2 = Ph) did react with ketones and gave excellent yields of the vinyl sulphides (18) (Table 3). The substituted



(9) (18) (19)

reagents also react with ketones if a methylthio instead of phenylthio group is present (9; R^1 = alkyl, R^2 = Me) and the substituent (R^1) is not branched (Table 3). Thus while (9; R^1 = Me, Et, R^2 = Me) gave good

TABLE 3

Synthesis of vinyl sulphides from phosphine oxides (9) and ketones

	R^1	R^2	R^3	R^4	Yield (%) of vinyl sulphide (18)
1.	Et	Ph	Ph	Me	*a*
2.	Et	Ph	$[CH_2]_5$		*a*
3.	H	Ph	Ph	Me	90
4.	H	Ph	$[CH_2]_5$		90
5.	Me	Me	$PhCH_2$	Me	72 [b]
6.	Pr^i	Me	$[CH_2]_5$		*a*
7.	Et	Me	Ph	Me	*a*
8.	Et	Me	$[CH_2]_5$		63 [c]

[a] No reaction. [b] Yield of ketone (19), 60%. [c] Based on starting material consumed. Yield of ketone (19) 60%.

yields of vinyl sulphides with ketones, (9; R^1 = Pr^i, R^2 = Me) did not react. In fact (9; R^1 = Et, R^2 = Me) was unchanged when treated with the very readily enolisable ketone acetophenone, a point also noted by Corey.[7] We are therefore still unable to make ketones branched on *both* sides of the carbonyl group by these methods. Ketones branched on one side can be made either by treating a branched reagent (9; R^1 = secondary alkyl) (Table 2) with an aldehyde, or an unbranched reagent (9; R^1 = primary alkyl, R^2 = Me) (Table 3) with a ketone.

Hydrolysis of Vinyl Sulphides.—The very multiplicity of methods available for this deceptively simple step [*i.e.* (18) to (19)] shows how troublesome it can be. The main methods are those based on mercury,[7,17,27] or titanium,[28,29] and the acid-catalysed addition of thiols followed by hydrolysis of the thioacetal.[20,30] Other workers have used various acids without heavy metal salts.[12,31,32] Most of the vinyl sulphides we have made can be hydrolysed simply and in high yield by dissolving them in chloroform containing trifluoroacetic acid (TFA) and working up with aqueous sodium carbonate.* This method gives poor results for the vinyl sulphides of aldehydes (18; R^1 = H) for which the HCl-catalysed addition of PhSH is better.[20] However, even this method fails for aldehyde derivatives where the double bond is stabilised by conjugation with an aromatic system (*e.g.* entry 6, Table 2). Vinyl sulphides of aldehydes have also been hydrolysed to the corresponding 2-phenylthio-aldehydes.[15] The only reported hydrolyses of dienyl sulphides to enones have been to give Δ^4-3-oxosteroids.[33] All the methods we tried with one diene (entry 5, Table 2)—TFA, $HgCl_2$, $TiCl_4$, HCl in MeOH—gave either unchanged starting material or uncharacterised decomposition products. There is clearly still a need for a more reliable general method for vinyl sulphide hydrolysis.

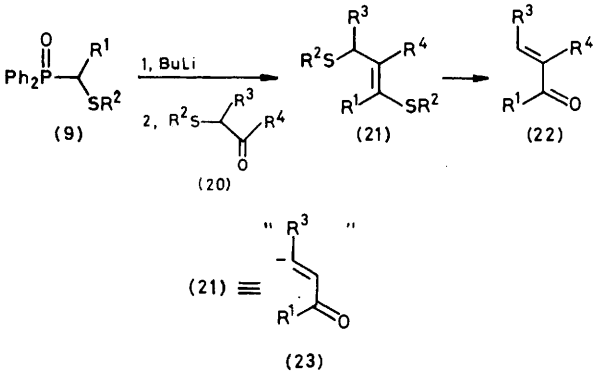
Enone Synthesis.—The hydrolysis of α,γ-bis(methylthio)- and -(phenylthio)-allyl compounds [*e.g.* (21)] to enones [*e.g.* (22)] has been reported where R^2 = Me [34] or Ph.[35] The bis(phenylthio)allyl compounds are also synthetically useful as 'reverse Michael equivalents' (23).[35] These compounds could obviously be made from our reagents (9) providing that they would react with the α-phenylthiocarbonyl compounds (20) and that the latter are available. We have already reported [36] a regiospecific and convergent synthesis of α-phenylthio-ketones from bis(phenylthio)-compounds (24) and we have now found that α-phenylthio-aldehydes may be made from the readily available α-phenylthio-esters (25) by reduction [37] to the alcohol (26) and oxidation with Corey's pyridinium chlorochromate reagent.[38]

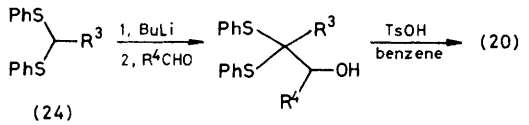
1,3-Bis(phenylthio)allyl ethers (21) can be prepared

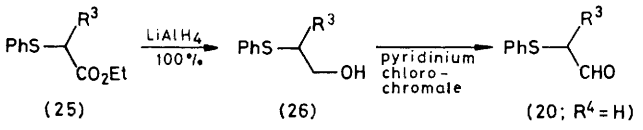
* Hydrolysis with TFA is mentioned also by R. C. Cookson and P. J. Parsons, *J.C.S. Chem. Comm.*, 1976, 990.

[27] S. Weiland and J. F. Arens, *Rec. Trav. chim.*, 1960, **79**, 1293.
[28] T. Mukaiyama, K. Kamio, S. Kobayashi, and H. Takei, *Bull. Chem. Soc. Japan*, 1972, **45**, 3723.
[29] T. Mukaiyama, M. Shiono, and T. Sato, *Chem. Letters*, 1974, 37.
[30] K. Geiss, B. Seuring, R. Pieter, and D. Seebach, *Angew. Chem. Internat. Edn.*, 1974, **13**, 479.
[31] B. S. Kupin and A. A. Petrov, *Zhur. org. Khim.*, 1967, **3**, 975 (*Chem. Abs.*, 1967, **67**, 99786).
[32] A. S. Kende, D. Constantinides, S. J. Lee, and L. Liebeskind, *Tetrahedron Letters*, 1975, 405.
[33] S. Bernstein and L. Dorfman, *J. Amer. Chem. Soc.*, 1946, **68**, 1152; G. Rosenkranz, S. Kaufmann and J. Romo, *ibid.*, 1949, **71**, 3689.
[34] E. J. Corey, B. W. Erickson, and R. Noyori, *J. Amer. Chem. Soc.*, 1971, **93**, 1724.
[35] T. Cohen, D. A. Bennett, and A. J. Mura, *J. Org. Chem.*, 1976, **41**, 2506.
[36] P. Blatcher and S. Warren, *J.C.S. Chem. Comm.*, 1976, 1055.
[37] P. Brownbridge, I. Fleming, A. Pearce, and S. Warren, *J.C.S. Chem. Comm.*, 1976, 751.
[38] E. J. Corey and J. W. Suggs, *Tetrahedron Letters*, 1975, 2647.

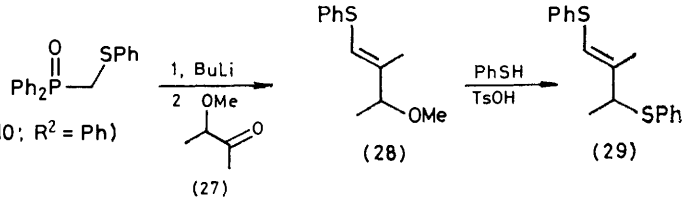
by our route in good yields (Table 4) on the basis of starting material consumed. Corey [34] made 1,3-bis-(methylthio)propene by the Wittig reaction of diethyl







methylthiomethylphosphonate and (methylthio)acetaldehyde, but achieved only 31% yield. We reasoned that a 1,3-disubstituted allyl system could be made more conveniently by using a starting ketone with a less acidic α-hydrogen atom. The α-methoxy-ketone (27) [39] reacted in very high yield with the phosphine oxide (10; R^2 = Ph) to give the α-phenylthio-γ-methoxyallyl compound (28), which underwent ready substitution on heating with benzenethiol and a catalytic amount of toluene-*p*-sulphonic acid monohydrate (TsOH), giving in much higher overall yield the α,γ-bis(phenylthio)allyl compound (29) already prepared (Table 4, entry 3).



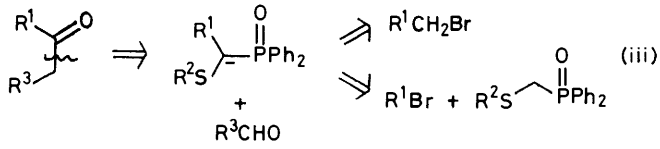


TABLE 4

Synthesis of enone precursors (21) from α-phenylthiocarbonyl compounds (20)

	R^1	R^2	R^3	R^4	Yield [a] (%)	Conversion (%)
1.	H	Ph	Et	H	76	48
2.	Et	Ph	Et	H	68	35
3.	H	Ph	Me	Me	76	51
4.	H	Ph	Me	Me	93 [b]	93 [b]

[a] Based on starting material consumed. [b] Overall yield *via* (28).

Retrosynthetic Analysis [40] *of the Routes to Ketones and Enones.*—These ketone syntheses [equation (iii)] clearly belong to the acyl anion family, but the acyl anion fragment can be derived either from an entire alkyl halide or by alkylation of the one-carbon unit (10). The method is iterative as the carbonyl fragment can itself be made by the same reaction sequence.

The enones are also derived from carbonyl compounds and alkyl halides; here the disconnections are those shown in equation (iv). This is in contrast to Cohen's enone equivalent,[35] where the starting material is itself an enone (30). After conversion into the α,γ-bis(phenylthio)allyl compound, and alkylation, hydrolysis gives the enone (31) functionalised at the γ-position. As the starting enone may be obtained by an aldol-type condensation, the disconnections corresponding to Cohen's route are those shown in equation (v). The two enone syntheses are thus complementary.

(iii)

Though we have in fairness emphasised the difficulties we found with some classes of compound, we believe that this route offers one of the easiest and highest yielding convergent routes to ordinary ketones that is at present available.

EXPERIMENTAL

General procedures have been described elsewhere.[41] N.m.r. signals marked with an asterisk belong to diastereotopic groups of protons. TFA refers to trifluoroacetic acid, TMEDA to tetramethylethylenediamine, THF to tetrahydrofuran (distilled from lithium aluminium hydride), and petrol to light petroleum (b.p. 60—80 °C). Reactions with butyl-lithium were carried out under nitrogen.

Diphenyl(phenylthiomethyl)phosphine Oxide [25] (10; R^2 =

[39] D. Guillerm-Drom, M. L. Capmau, and W. Chodkiewicz, *Bull. Soc. chim. France* (*B*), 1973, 1417.

[40] I. Fleming, 'Selected Organic Syntheses,' London, Wiley, 1973, pp. 1—6; E. J. Corey, *Pure Appl. Chem.*, 1967, **14**, 19.

[41] A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden, and S. Warren, *J.C.S. Perkin I*, 1977, 550.

Ph).—*Method B*. Ethyl diphenylphosphinite [42] (24 g) and chloromethyl phenyl sulphide [43] (17.5 g) were heated together under nitrogen at 150 °C for 1.5 h. On cooling, a solid separated, which was recrystallised from ethyl acetate–petrol to give the phosphine oxide (32.5 g, 96%), m.p. 106—107 °C (lit.,[25] 101—102 °C), R_F (EtOAc) 0.40, τ ($CDCl_3$) 2.1—2.9 (15 H, m, Ph_2P and PhS) and 6.27 (2 H, d, J_{HP} 9 Hz, CH_2P), *m/e* 324 (M^+, 42%), 279 (Ph_3POH, 18), and 201 (Ph_2PO, 100).

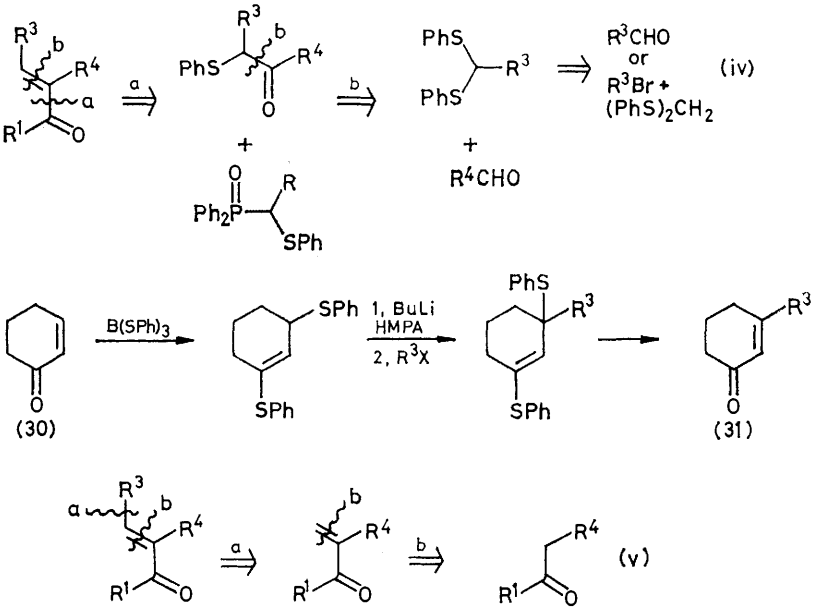
Diphenyl(methylthiomethyl)phosphine Oxide [25,26] (10; R^2 = Me).—Reaction of ethyl diphenylphosphinite [42] (10.6 g) and chloromethylmethyl sulphide (4.55 g) (method B) gave the phosphine oxide (10.4 g, 86%), m.p. 139—140 °C (from EtOAc–petrol) (lit.,[25] 139—140 °C), R_F (EtOAc) 0.20. Spectra agree with those reported.[26]

Diphenyl-1-(phenylthio)ethylphosphine Oxide (9; R^1 = Me, R^2 = Ph).—*Method C*. Diphenyl(phenylthiomethyl)-phosphine oxide (0.7 g, 2.2 mmol) in dry THF (30 ml) and TMEDA (0.35 ml, 2.5 mmol) was treated with n-butyl-lithium (1.05 ml; 2.4M in hexane) at −78 °C. The orange anion was quenched after 0.2 h with methyl iodide (0.16 ml, 2.5 mmol) and the resulting pale yellow solution was allowed to warm to room temperature over 0.5 h. Aqueous ammonium chloride (40 ml) was added, and the product extracted with chloroform (3 × 30 ml). The organic extracts were washed with dilute hydrochloric acid (20 ml), dried ($MgSO_4$), and evaporated to give a pale yellow solid. Recrystallisation (ethyl acetate–petrol) gave the *phosphine oxide* (490 mg, 69%), m.p. 154—155 °C, R_F (EtOAc) 0.41, $\nu_{max.}$ ($CHCl_3$) 1 580, 1 480 (PhS), 1 440 (PhP), and 1 180 cm^{-1} (P=O), τ 2.0—2.6 (10 H, m, Ph_2P), 2.8 (5 H, m, PhS), 6.62 (1 H, dq, J_{HP} 9 Hz, J_{HH} 7.5 Hz, MeC*H*P), and 8.46 (3 H, dd, J_{HP} 15 Hz, J_{HH} 7.5 Hz, CH_3CHP), *m/e* 338 (M^+, 25%), 279 (Ph_3POH, 22), 202 (Ph_2POH, 100), 201 (Ph_2PO, 50), 138 (PhSEt, 80), and 110 (PhSH, 50) (Found: C, 71.2; H, 5.95; P, 9.35. $C_{20}H_{19}OSP$ requires C, 71.0; H, 5.65; P, 9.15%).

1-(Methylthio)ethyldiphenylphosphine Oxide (9; R^1 = R^2 = Me).—Reaction of (methylthiomethyl)diphenylphosphine oxide (2 g, 7.6 mmol), n-butyl-lithium (4.6 ml; 1.8M in hexane), TMEDA (1.15 ml, 8.3 mmol), and methyl iodide (0.52 ml, 8.3 mmol) (method C) gave a pale yellow solid. Recrystallisation (ethyl acetate–petrol) gave the *phosphine oxide* (1.57 g, 75%), m.p. 122—123 °C, R_F (EtOAc) 0.30, $\nu_{max.}$ ($CHCl_3$) 1 440 (PPh) and 1 185 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.7 (10 H, m, Ph_2P), 6.76 (1 H, quint, J_{HP} = J_{HH} = 7.5 Hz, MeC*H*P), 7.93 (3 H, s, MeS), and 8.50 (3 H, dd, J_{HP} 15, J_{HH} 7.5 Hz, CH_3CHP), *m/e* 276 (M^+, 10%), 230 (M − MeSH, 100), and 202 (Ph_2POH, 85%) (Found: C, 64.9; H, 6.1; P, 11.0. $C_{15}H_{17}OPS$ requires C, 65.2; H, 6.2; P, 11.2%).

Diphenyl-1-(phenylthio)propylphosphine Oxide (9; R^1 = Et, R^2 = Ph).—*Method A*. Diphenylpropylphosphine oxide [41] (1.5 g, 6.1 mmol) in dry THF (40 ml) and TMEDA (0.93 ml, 6.7 mmol) was treated with n-butyl-lithium (2.8 ml; 2.4M in hexane) at −78 °C. After 0.2 h the orange anion was added to a solution of diphenyl disulphide (1.37 g, 6.3 mmol) in dry THF (30 ml) at −78 °C and the resulting pale yellow solution was quickly worked up with aqueous sodium carbonate. The product was extracted with chloroform (3 × 30 ml) and the organic extracts were washed with dilute hydrochloric acid (20 ml) and saturated brine (20 ml), dried ($MgSO_4$), and evaporated. Recrystallisation from cyclohexane gave the *phosphine oxide* (1.59 g, 73%), m.p. 140—141 °C, R_F (EtOAc) 0.41, $\nu_{max.}$ ($CHCl_3$) 1 580, 1 480 (PhS), 1 438 (PhP), and 1 175 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.7 (10 H, m, Ph_2P), 2.85 (5 H, s, PhS), 6.49 (1 H, dt, J_{HH} 9.5, J_{HP} 2 Hz, CH_2·C*H*P), 7.8—8.4 (2 H, m, CH_2), and 8.79 (3 H, t, J_{HH} 7 Hz, CH_3CH_2), *m/e* 352 (M^+, 20%), 279 (Ph_3POH, 38), 243 (M − PhS, 45), 202 (Ph_2POH, 100), 151 (M − Ph_2PO, 97), 109 (PhS, 65), and 77 (Ph, 71) (Found: M^+, 351.1049. $C_{21}H_{21}OPS$ requires M, 352.1050).

1-(Methylthio)propyldiphenylphosphine Oxide (9; R^1 =



[42] P. F. Cann, D. Howells, and S. Warren, *J.C.S. Perkin II*, 1972, 304.

[43] L. W. Fancher, Ger. Pat. 1,112,735 (*Chem. Abs.*, 1962, **56**, 11499).

Et, R^2 = Me).—Diphenylpropylphosphine oxide [41] (3 g, 12.3 mmol), n-butyl-lithium (7.8 ml; 1.8M in hexane), TMEDA (1.95 ml, 14 mmol), and dimethyl disulphide (1.27 ml, 14 mmol) (method A; work-up with aqueous 3M-sodium hydroxide) gave the *phosphine oxide* (2.22 g, 62%), m.p. 148—150 °C (from ethyl acetate–petrol), R_F (EtOAc) 0.33, $\nu_{max.}$ ($CHCl_3$) 1 440 (PPh) and 1 180 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, Ph_2P), 7.08 (1 H, ddd, J_{HP} 11, J_{HH} 8, 4 Hz, CH_2*CHP), 7.9—8.4 (2 H, m, CH_2*CHP) overlain by 7.98 (3 H, s, MeS), and 8.87 (3 H, t, J_{HH} 7 Hz, CH_3CH_2), *m/e* 290 (M^+, 20%), 244 (Ph_2POPr, 100), 229 ($Ph_2POCH_2CH_2$, 50), 202 (Ph_2PO, 96), and 89 (M − Ph_2PO, 73) (Found: C, 66.2; H, 6.75; P, 10.5. $C_{16}H_{19}OPS$ requires C, 66.2; H, 6.6; P, 10.7%).

(2-*Methyl*-1-*phenylthiopropyl*)*diphenylphosphine Oxide* (9; R^1 = Pr^i, R^2 = Ph).—Isobutyldiphenylphosphine oxide [41] (3 g, 11.6 mmol), n-butyl-lithium (5.2 ml; 2.4M in hexane), TMEDA (1.8 ml, 12.5 mmol), and diphenyl disulphide (2.6 g, 11.9 mmol) (method A) gave the *phosphine oxide* (3.36 g, 81%), m.p. 180—182 °C (from ethyl acetate), R_F (EtOAc) 0.47, $\nu_{max.}$ ($CHCl_3$) 1 580, 1 480 (PhS), 1 440 (PhP), and 1 175 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.8 (10 H, m, Ph_2P), 2.9—3.1 (5 H, m, PhS), 6.42 (1 H, dd, J_{HP} 9, J_{HH} 3 Hz, CHCHP), 7.4—7.8 (1 H, m, Me_2CHCHP), and 8.78 and 8.90 (each 3 H, d, J_{HH} 7 Hz, Me_2*C), *m/e* 366 (M^+, 17%), 279 (Ph_3POH, 53), 257 (M − PhS, 70), 202 (Ph_2POH, 85), and 165 (M − Ph_2PO, 100) (Found: C, 72.3; H, 6.5; P, 8.2. $C_{22}H_{23}OPS$ requires C, 72.1; H, 6.3; P, 8.45%).

(2-*Methyl*-1-*methylthiopropyl*)*diphenylphosphine Oxide* (9; R^1 = Pr^i, R^2 = Me).—Isobutyldiphenylphosphine oxide [41] (1.5 g, 5.8 mmol), n-butyl-lithium (2.7 ml; 2.4M in hexane), TMEDA (0.9 ml, 6.4 mmol), and dimethyl disulphide (0.58 ml, 6.4 mmol) (method A, work-up with aqueous 3M-sodium hydroxide) gave the *phosphine oxide* (1.39 g, 78%), m.p. 194—195 °C (from ethyl acetate), R_F (EtOAc) 0.46, $\nu_{max.}$ ($CHCl_3$) 1 440 (PhP) and 1 182 cm^{-1} (P=O), τ ($CDCl_3$) 1.9—2.6 (10 H, m, Ph_2P), 7.04 (1 H, dd, J_{HP} 11, J_{HH} 3 Hz, CHCHP), 7.3—7.8 (1 H, m, Me_2CHCHP), and 8.86 and 9.00 (each 3 H, d, J_{HH} 7 Hz, Me_2*C), *m/e* 304 (M^+, 7%), 258 (M − MeSH, 60), 243 [$Ph_2P(O)\cdot C_3H_4$, 100], 201 (Ph_2PO, 70), 103 (M − Ph_2PO, 30), and 77 (30) (Found: C, 66.8; H, 7.0; P, 10.35. $C_{17}H_{21}OPS$ requires C, 67.1; H, 6.95; P, 10.2%).

Diphenyl-(2-*phenyl*-1-*phenylthioethyl*)*phosphine Oxide* (9; R^1 = $PhCH_2$, R^2 = Ph).—(a) *By sulphenylation*. Phenethyldiphenylphosphine oxide [44] (1 g, 3.3 mmol), n-butyl-lithium (1.5 ml; 2.4M in hexane), TMEDA (0.5 ml, 3.6 mmol), and diphenyl disulphide (0.74 g, 3.4 mmol) (method A) gave the *phosphine oxide* (1.07 g, 79%), m.p. 178—179 °C (from ethyl acetate–petrol), R_F (EtOAc) 0.40, $\nu_{max.}$ ($CHCl_3$) 1 580, 1 480 (Ph), 1 438 (PhP), and 1 175 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, Ph_2P), 2.75 (5 H, s, PhS), 2.9—3.5 (5 H, m, Ph), and 6.2—7.3 (3 H, m, $PCHCH_2$), *m/e* 414 (M^+, 8%), 305 (M − PhS, 100), 212 (M − Ph_2POH, 80), and 202 (Ph_2POH, 92) (Found: C, 75.0; H, 5.65; P, 7.25. $C_{26}H_{23}OPS$ requires C, 75.3; H, 5.6; P, 7.45%).

(b) *By alkylation*. Diphenyl(phenylthiomethyl)phosphine oxide (0.5 g, 1.55 mmol), n-butyl-lithium (0.8 ml; 2.4M in hexane), TMEDA (0.27 ml, 1.9 mmol), and benzyl bromide (0.23 ml, 1.9 mmol) (method C) gave the same phosphine oxide (0.54 g, 84%).

Bis(*phenylthio*)*methyldiphenylphosphine Oxide* (11).—Diphenyl(phenylthiomethyl)phosphine oxide (2 g, 6.2 mmol) in dry THF (40 ml) and TMEDA (1 ml, 7 mmol) was treated with n-butyl-lithium (3.9 ml; 1.8M in hexane) at −78 °C. After 0.2 h, the orange anion was added to a solution of diphenyl disulphide (1.55 g, 7 mmol) in dry THF (30 ml) at −78 °C, and the resulting pale yellow solution was quickly worked up with aqueous sodium carbonate. The product was extracted with chloroform (3 × 40 ml), and the organic extracts were washed with dilute hydrochloric acid (20 ml), dried ($MgSO_4$), and evaporated to give a white solid. Recrystallisation from ethyl acetate–petrol gave the *phosphine oxide* (2.0 g, 75%), m.p. 152—153 °C, R_F (EtOAc) 0.55, $\nu_{max.}$ ($CHCl_3$) 1 580, 1 480 (PhS), 1 440 (PhP), and 1 185 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, Ph_2P), 2.8 (10 H, s, PhS), and 5.14 (1 H, d, J_{HP} 10 Hz, CHP), *m/e* 432 (M^+, 12%), 323 (M − PhS, 48), 231 (M − Ph_2PO, 100), 201 (Ph_2PO, 42), 199 (PhSCHPh, 40), and 109 (PhS, 80) (Found: C, 69.1; H, 4.9; P, 6.9. $C_{25}H_{21}OPS_2$ requires C, 69.4; H, 4.9; P, 7.15%).

1-*Phenyl*-2-*phenylthiobut*-1-*ene* (14; R^1 = Et, R^2 = R^3 = Ph).—Diphenyl-1-(phenylthio)propylphosphine oxide (300 mg, 0.85 mmol) in dry THF (30 ml) was treated with n-butyl-lithium (0.56 ml; 1.8M in hexane) at −78 °C for 0.2 h. The yellow anion was quenched with benzaldehyde (0.1 ml, 1 mmol) to give a colourless solution which was allowed to warm to room temperature during 0.5 h. A thick white precipitate formed (diphenylphosphinic acid) which was dissolved by the addition of aqueous ammonium chloride (20 ml), and the product was extracted with chloroform (3 × 30 ml). The organic extracts were dried ($MgSO_4$) and evaporated, and the resulting oil was purified by preparative t.l.c. (CH_2Cl_2) to give a 4 : 3 mixture of geometric isomers of the *vinyl sulphide* (190 mg, 93%), as an oil, R_F (CH_2Cl_2) 0.77, $\nu_{max.}$ ($CHCl_3$) 1 610 (C=C), 1 600, 1 580, and 1 490 cm^{-1} (Ph), τ ($CDCl_3$) 2.4—2.9 (10 H, m, Ph and PhS), 3.20 and 3.30 (1 H, two s, ratio 3 : 4, CH=C), 7.54 and 7.68 (2 H, two q, J 7 Hz, $MeCH_2C$=C), and 8.78 and 8.85 (3 H, two t, J 7 Hz, Me), *m/e* 240 (M^+, 80), 165 (M − EtCS, 42), 106 (PhEt, 100), and 78 (73) (Found: M^+, 240.0965. $C_{16}H_{16}S$ requires M, 240.0972).

1-*Phenyl*-2-*phenylthionon*-2-*ene* (14; R^1 = $PhCH_2$, R^2 = Ph, R^3 = n-C_6H_{13}).—By a method similar to that described above, diphenyl-(2-phenyl-1-phenylthioethyl)phosphine oxide (0.4 g, 0.97 mmol), n-butyl-lithium (0.5 ml; 2.4M in hexane), and n-heptanal (0.14 ml, 1.1 mmol) gave an oil, which after preparative t.l.c. (CH_2Cl_2) gave a 2 : 1 mixture of geometric isomers of the *vinyl sulphide* (280 mg, 93%) as an oil, R_F (CH_2Cl_2) 0.77, $\nu_{max.}$ ($CHCl_3$) 1 580, 1 490 (Ph), and 1 470 cm^{-1} (PhS), τ ($CDCl_3$) 2.6—3.0 (10 H, m, PhS and Ph), 3.98 and 4.10 (1 H, t, J 8, and t, J 7 Hz, CH_2–CH=C), 6.43 and 6.52 (2 H, two s, ratio 1 : 2, $PhCH_2$), 7.5—7.9 (2 H, m, allyl CH_2), 8.4—8.9 (8 H, m, $[CH_2]_4$), and 9.0—9.2 (3 H, m, Me), *m/e* 310 (M^+, 43%), 239 (M − C_5H_{11}, 14), 129 ($C_6H_{11}CS$, 100), and 109 (PhS, 47) (Found: M^+, 310.1746. $C_{21}H_{26}S$ requires M, 310.1754).

1,3-*Diphenyl*-2-*phenylthiopropene* (14; R^1 = $PhCH_2$, R^2 = R^3 = Ph).—In the same way, diphenyl-(2-phenyl-1-phenylthioethyl)phosphine oxide (0.4 g, 0.97 mmol), n-butyl-lithium (0.46 ml, 1.1 mmol) and benzaldehyde (0.11 ml, 1.1 mmol), gave an oil, which after preparative t.l.c. (CH_2Cl_2) gave a 3 : 1 mixture of geometric isomers of the *vinyl sulphide* (261 mg, 90%), m.p. 60—63 °C, R_F (CH_2Cl_2) 0.85, $\nu_{max.}$ ($CHCl_3$) 1 600, 1 580, 1 490 (Ph), and 1 470 cm^{-1} (PhS), τ ($CDCl_3$) 2.4—3.0 (15 H, m, Ph and

[44] J. I. Grayson, H. K. Norrish, and S. Warren, *J.C.S. Perkin I*, 1976, 2556.

PhS), 3.18 and 3.27 (1 H, two s, CH=C), and 6.21 and 6.44 (2 H, two s, ratio 3 : 1, $PhCH_2$), *m/e* 302 (M^+, 36%), 214 ($PhCHCH_2SPh$, 63), and 123 ($PhSCH_2$, 100) (Found: M^+, 302.1146. $C_{21}H_{18}S$ requires *M*, 302.1128).

1-(p-*Methoxyphenyl*)-3-*methyl*-2-*phenylthiobut*-1-*ene* (14; $R^1 = Pr^i$, R^2 = Ph, $R^3 = p$-MeO·C_6H_4).—In the same way, (2-methyl-1-phenylthiopropyl)diphenylphosphine oxide (0.6 g, 1.65 mmol), n-butyl-lithium (0.75 ml; 2.4M in hexane), and *p*-methoxybenzaldehyde (0.22 ml, 1.8 mmol) gave an oil, which after preparative t.l.c. (CH_2Cl_2) gave a 1 : 1 mixture of geometric isomers of the *vinyl sulphide* (436 mg, 94%), as an oil, R_F (CH_2Cl_2) 0.73, $\nu_{max.}$ ($CHCl_3$) 1 600, 1 580, 1 500 (Ph), and 1 250 cm^{-1} (MeO), τ ($CDCl_3$) 2.4—3.2 (9.5 H, m, aryl H and CH=C of one isomer), 3.6 (0.5 H, s, CH=C of other isomer), 6.24 and 6.26 (3 H, two s, 1 : 1 ratio, MeO), 6.65 and 7.4 (1 H, two septets, *J* 7 Hz, Me_2CH), and 8.80 (6 H, d, *J* 7 Hz, Me_2C), *m/e* 284 (M^+, 100%), 175 (*M* — PhS, 85), and 160 (*M* — PhS — Me, 47) (Found: M^+, 284.1224. $C_{18}H_{20}OS$ requires *M*, 284.1235).

5-*Methyl*-1-*phenyl*-4-*phenylthiohexa*-1,3-*diene* (14; $R^1 = Pr^i$, R^2 = Ph, R^3 = PhCH=CH).—In the same way (2-methyl-1-phenylthiopropyl)diphenylphosphine oxide (0.7 g, 1.9 mmol), n-butyl-lithium (0.19 ml; 2.4M in hexane), and cinnamaldehyde (0.26 ml, 2.1 mmol) gave an oil, which after preparative t.l.c. (CH_2Cl_2) gave a 2 : 1 mixture of geometric isomers of the *dienyl sulphide* (496 mg, 93%), as an oil, R_F (CH_2Cl_2) 0.79, $\nu_{max.}$ ($CHCl_3$) 1 650, 1 610 (C=C), and 1 580 and 1 480 cm^{-1} (Ph), τ ($CDCl_3$) 2.4—3.1 (11 H, m, Ph_2 and PhCH=C*H*–CH=C), 3.52 and 4.02 (1 H, d, *J* 10, and d, *J* 11 Hz, PhCH=CH–C*H*=C), 3.55 and 3.69 (1 H, d, *J* 16, and d, *J* 15 Hz, *trans*-PhC*H*=CH), 6.68 and 7.47 (1 H, two septets, *J* 7 Hz, ratio 1 : 2, Me_2CH), and 8.76 and 8.83 (6 H, two d, *J* 7 Hz, Me_2C), *m/e* 280 (M^+, 90%), 203 (*M* — Ph, 35), 170 (*M* — PhSH, 80), 155 (*M* — PhSH — Me, 100), and 91 (60) (Found: M^+, 280.1280. $C_{19}H_{20}S$ requires *M*, 280.1285).

1-(3,4-*Methylenedioxyphenyl*)-2-*phenylthioethene* [14; R^1 = H, R^2 = Ph, R^3 = 3,4-$(CH_2O_2)C_6H_3$].—In the same way diphenylphenylthiomethylphosphine oxide (0.7 g, 2.16 mmol), n-butyl-lithium (1 ml; 2.4M in hexane), and piperonal (0.36 g, 2.4 mmol) gave an oil, which after preparative t.l.c. (CH_2Cl_2) gave a 4 : 1 mixture of geometric isomers of the *vinyl sulphide* (507 mg, 92%), as an oil, R_F (CH_2Cl_2) 0.77, τ ($CDCl_3$) 2.6—2.9 (5 H, m, PhS), 3.2—3.7 (5 H, m, aryl and vinyl H), and 4.16 and 4.18 (2 H, two s, ratio 1 : 4, OCH_2O), *m/e* 256 (M^+, 100%), 149 (62), 121 (*M* — PhSCH=CH, 32), and 110 (PhSH, 28) (Found: M^+, 256.0544. $C_{15}H_{12}O_2S$ requires *M*, 256.0557).

1-*Phenylbutan*-2-*one* (17; R^1 = Et, R^3 = Ph).—1-Phenyl-2-phenylthiobut-1-ene (160 mg) was dissolved in TFA (3 ml) and chloroform (3 ml) and stirred at room temperature for 0.3 h. The mixture was neutralised with aqueous sodium carbonate and extracted with chloroform (3 × 20 ml); the extract was dried ($MgSO_4$) and evaporated to give an oil. Bulb-to-bulb distillation gave the ketone (76 mg, 78%), b.p. 70—80 °C at 0.05 mmHg (lit.,[45] b.p. 230 °C), $\nu_{max.}$ (film) 1 710 (C=O), 1 600, 1 580, and 1 490 cm^{-1} (Ph), τ ($CDCl_3$) 2.8 (5 H, m, Ph), 6.4 (2 H, s, CH_2Ph), 7.6 (2 H, q, *J* 7 Hz, CH_2Me), and 9.0 (3 H, t, *J* 7 Hz, CH_3CH_2).

1-*Phenylnonan*-2-*one* (17; $R^1 = PhCH_2$, $R^3 = n\text{-}C_6H_{13}$).—In a similar way, 1-phenyl-2-phenylthionon-2-ene (204 mg), TFA (3 ml), and chloroform (3 ml) gave the ketone (133 mg, 93%) after bulb-to-bulb distillation, b.p. 75—80 °C at 0.05 mmHg (lit.,[46] 100—104 °C at 0.3 mmHg), $\nu_{max.}$ ($CHCl_3$) 1 705 cm^{-1} (C=O), τ ($CDCl_3$) 2.6—3.0 (5 H, m, Ph), 6.37 (2 H, s, CH_2Ph), 7.60 (2 H, t, *J* 7.5 Hz, CH_2CH_2CO), 8.3—8.8 (10 H, m, $[CH_2]_5$), and 9.16 (3 H, t, *J* 5 Hz, Me), *m/e* 218 (M^+, 5%), 127 (*M* — $PhCH_2$, 100), and 92 ($PhCH_3$, 35).

1,3-*Diphenylpropan*-2-*one* (17; $R^1 = PhCH_2$, R^3 = Ph).—In a similar way, 1,3-diphenyl-2-phenylthiopropene (204 mg), TFA (3 ml), and chloroform (3 ml) gave the ketone (137 mg, 97%), after bulb-to-bulb distillation, b.p 90—100 °C at 0.05 mmHg (lit.,[45] 112—125 °C at 0.1 mmHg), $\nu_{max.}$ ($CHCl_3$) 1 710 (C=O), 1 600, 1 580, and 1 480 cm^{-1} (Ph), τ ($CDCl_3$) 2.6—2.8 (10 H, m, Ph) and 6.35 (4 H, s, CH_2).

1-(p-*Methoxyphenyl*)-3-*methylbutan*-2-*one* (17; $R^1 = Pr^i$, $R^3 = p$-MeO·C_6H_4).—In a similar way, 1-(*p*-methoxyphenyl)-3-methyl-2-phenylthiobut-1-ene (436 mg), TFA (5 ml), and chloroform (5 ml), stirred for 4 h at room temperature, gave the ketone (252 mg, 86%), after bulb-to-bulb distillation, b.p. 90—100° C at 0.05 mmHg (lit.,[47] 146—152 °C at 10 mmHg), $\nu_{max.}$ ($CHCl_3$) 1 705 (C=O), 1 610, 1 505 (Ph), and 1 240 and 1 035 cm^{-1} (OMe), τ ($CDCl_3$) 2.8—3.2 (4 H, q, A_2B_2, J_{AB} 8 Hz, separation 26 Hz, aryl H), 6.22 (3 H, s, MeO), 6.34 (2 H, s, CH_2), 7.50 (1 H, sept, *J* 7 Hz, Me_2CH), and 8.92 (6 H, d, *J* 7 Hz, Me_2C), *m/e* 192 (M^+, 100%) and 121 (MeO·$C_6H_4CH_2$, 37) (Found: M^+, 192.1150. $C_{13}H_{16}O_2$ requires *M*, 192.1150).

Attempted Hydrolyses of 5-*Methyl*-1-*phenyl*-4-*phenylthiohexa*-1,3-*diene* (14; $R^1 = Pr^i$, R^2 = Ph, R^3 = PhCH=CH).—The dienyl sulphide (200 mg) was treated under reflux with concentrated hydrochloric acid (1 ml) in methanol (70 ml) for 18 h. Evaporation, and examination of the residue by t.l.c. and n.m.r. showed no reaction had taken place. Similarly, heating the dienyl sulphide (249 mg) with mercury(II) chloride (490 mg) in 3 : 1 acetonitrile–water (20 ml) under reflux for 72 h, gave unchanged dienyl sulphide (170 mg, 68% after preparative t.l.c.) as the only identified product. Similarly, stirring the dienyl sulphide (402 mg) with titanium tetrachloride (0.5 ml) in acetonitrile (10 ml) at room temperature for 5 h, followed by preparative t.l.c. gave only starting material (142 mg, 35%). The dienyl sulphide (203 mg) dissolved in TFA–chloroform to give a dark red solution. After stirring for 2 h, isolation of the product gave a yellow oil (196 mg), which appeared (n.m.r., t.l.c., i.r.) to be a mixture of decomposition products. No trace of the expected enone or of starting material was found.

2-*Phenyl*-1-*phenylthiopropene* [29,48] (18; R^1 = H, R^2 = R^3 = Ph, R^4 = Me).—Diphenyl(phenylthiomethyl)phosphine oxide (0.7 g, 2.15 mmol), in dry THF (30 ml) was treated with n-butyl-lithium (1 ml; 2.4M in hexane) at −78 °C. After 0.2 h, the orange anion was quenched with freshly distilled acetophenone (0.28 mg, 2.4 mmol). The mixture was allowed to warm to room temperature for 0.5 h; a thick white precipitate formed, which was dissolved by the addition of aqueous ammonium chloride. The product was extracted into chloroform (3 × 30 ml), and the organic extracts were dried ($MgSO_4$) and evaporated

[45] ' Handbook of Chemistry and Physics,' ed. R. C. Weast, C.R.C. Press, Cleveland, Ohio, 1975.

[46] R. B. Dran, P. Decock, and B. Decock-le-Reverend, *Compt. rend.*, 1971, **272C**, 1664.

[47] Knoll, A.G., Ger. Pat. 727 405/1938 (Beilstein, Handbuch der Organischen Chemie, **8**, III, 489).

[48] I. Kuwajima, S. Sato, and Y. Kurata, *Tetrahedron Letters*, 1972, 737.

to give an oil. Preparative t.l.c. (CH_2Cl_2) gave a 6 : 1 mixture of geometric isomers of the vinyl sulphide (436 mg, 90%), as an oil, R_F (CH_2Cl_2) 0.86, τ ($CDCl_3$) 2.6—2.9 (10 H, m, Ph_2), 3.44 and 3.74 (1 H, two m, ratio 6 : 1, CH=C), and 7.77 and 7.80 (3 H, two s, ratio 6 : 1, MeC=C), *m/e* 226 (M^+, 100%), 211 (M — Me, 14), 115 (32), and 91 (43).

Phenylthiomethylenecyclohexane [29,48,49] (18; R^1 = H, R^2 = Ph, R^3R^4 = $[CH_2]_5$).—In the same way diphenyl(phenylthiomethyl)phosphine oxide (0.5 g, 1.55 mmol), n-butyllithium (0.7 ml, 1.7 mmol) and freshly distilled cyclohexanone (0.18 ml, 1.7 mmol) gave an oil, which after preparative t.l.c. (CH_2Cl_2) gave the vinyl sulphide (284 mg, 90%), as an oil, R_F (CH_2Cl_2) 0.85. Spectroscopic data agree with those reported.[49]

2-*Methyl*-3-*methylthio*-1-*phenylbut*-2-*ene* (18; R^1 = R^2 = R^4 = Me, R^3 = $PhCH_2$).—In the same way, 1-(methylthio)ethyldiphenylphosphine oxide (0.5 g, 1.8 mmol), n-butyl-lithium (0.9 ml; 2.4M in hexane), and benzyl methyl ketone (0.28 ml, 2.1 mmol), gave an oil, which after preparative t.l.c. (CH_2Cl_2), gave a 1 : 1 mixture of geometric isomers of the *vinyl sulphide* (249 mg, 72%) as an oil, R_F (CH_2Cl_2) 0.75, $\nu_{max.}$ ($CHCl_3$) 1 600 and 1 480 cm^{-1} (Ph), τ ($CDCl_3$) 2.8 (5 H, m, Ph), 6.22 and 6.50 (2 H, two s, ratio 1 : 1, $PhCH_2$), 7.74 and 7.75 (3 H, two s, MeS), 7.88 and 7.94 (3 H, two q, J 1 Hz, MeC=), and 8.04 and 8.30 (3 H, two q, J 1 Hz, MeC=), *m/e* 192 (M^+, 100%), 145 (M — MeS, 60), 143 (60), 129 (56), and 91 (35) (Found: M^+, 192.0967. $C_{12}H_{16}S$ requires M, 192.0972).

(1-*Methylthiopropylidene*)*cyclohexane* (18; R^1 = Et, R^2 = Me, R^3R^4 = $[CH_2]_5$).—In the same way 1-(methylthio)-propyldiphenylphosphine oxide (0.7 g, 2.4 mmol), n-butyllithium (1.45 ml; 1.8M in hexane), TMEDA (0.37 ml, 2.6 mmol), and freshly distilled cyclohexanone (0.27 ml, 2.6 mmol) gave an oil. Preparative t.l.c. (CH_2Cl_2) gave starting material (253 mg, 36%), R_F (CH_2Cl_2) 0.0, and the *vinyl sulphide* (163 mg, 40% conversion, 63% based on starting material consumed) as an oil, R_F (CH_2Cl_2) 0.80, $\nu_{max.}$ ($CHCl_3$) 1 620 cm^{-1} (C=C), τ ($CDCl_3$) 7.4—7.6 (4 H, m, CH_2–C= on ring), 7.65 (2 H, q, J 7 Hz, =C–CH_2Me), 7.87 (3 H, s, MeS), 8.47 (6 H, m, $[CH_2]_3$), and 8.96 (3 H, t, J 7 Hz, CH_3CH_2), *m/e* 170 (M^+, 100%), 155 (M — Me, 95), 123 (M — MeS, 9), and 81 (14) (Found: M^+, 170.1131. $C_{10}H_{18}S$ requires M, 170.1128).

Reaction of Diphenyl-1-*phenylthiopropylphosphine Oxide with Ketones*.—The phosphine oxide (9; R^1 = Et, R^2 = Ph) (0.5 g, 1.43 mmol) in dry THF (30 ml) and TMEDA (0.23 ml, 1.6 mmol) was treated with n-butyl-lithium (0.67 ml, 1.6 mmol) at −78 °C. After 0.3 h, the orange anion was quenched with freshly distilled cyclohexanone. The resulting pale yellow solution was allowed to warm to room temperature for 0.5 h, but no precipitate formed. After work-up in the usual way, starting material was the only identifiable material obtained. Similarly, no reaction was observed with acetophenone, or if the reaction was carried out using n-butyl-lithium at room temperature, or using sodium hydride to form the anion.

3-*Methyl*-4-*phenylbutan*-2-*one* (19; R^1 = R^4 = Me, R^3 = $PhCH_2$).—2-Methyl-3-methylthio-1-phenylbut-2-ene (235 mg) was stirred with TFA (3 ml) and chloroform (3 ml) for 4 h at room temperature. The mixture was poured into aqueous sodium carbonate and extracted with chloroform (3 × 30 ml); the organic extracts were dried ($MgSO_4$) and evaporated to give an oil. Bulb-to-bulb distillation gave the ketone (116 mg), b.p. 120—130 °C at 0.1 mmHg (lit.,[50] b.p. 111 °C at 10 mmHg), $\nu_{max.}$ (film) 1 710 (C=O), 1 605, and 1 495 cm^{-1} (Ph), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 6.8—7.6 (3 H, m, $PhCH_2CHCO$), 7.92 (3 H, s, MeCO), and 8.90 (3 H, d, J 7 Hz, CH_3CH), *m/e* 162 (M^+, 35%), 147 (M — Me, 21), 119 (M — MeCO, 18), and 91 (C_7H_7 100).

Cyclohexyl Ethyl Ketone (19; R^1 = Et, R^3R^4 = $[CH_2]_5$).—By a method similar to that described above, 1-(methylthio)propylidenecyclohexane (225 mg), TFA (2 ml), and chloroform (2 ml) gave an oil, which after bulb-to-bulb distillation gave the ketone (108 mg, 60%), b.p. 80—90 °C at 15 mmHg (lit.,[51] b.p. 88—89 °C at 19 mmHg), $\nu_{max.}$ (film) 1 710 cm^{-1} (C=O), τ ($CDCl_3$) 7.54 (2 H, q, J 7 Hz, CH_2Me), 7.6—8.8 (11 H, m, cyclohexyl ring), and 8.96 (3 H, t, J 7 Hz, CH_3CH_2).

2-*Phenylthiobutanal* (20; R^3 = Et, R^4 = H).—2-Phenylthiobutan-1-ol [52] (0.48 g, 2.6 mmol), and pyridinium chlorochromate [38] (1.35 g, 6.3 mmol) were stirred at room temperature in dry dichloromethane (50 ml) for 2.5 h. The dark suspension was filtered and the solid washed well with ether. The filtrate was evaporated and the residue purified by preparative t.l.c. (3 : 7 acetone–petrol) to give the aldehyde † (260 mg, 55%), R_F (3 : 7 acetone–petrol) 0.44, $\nu_{max.}$ (film) 2 700 (CHO), 1 710 (C=O), and 1 580 cm^{-1} (PhS), τ ($CDCl_3$) 0.72 (1 H, d, J 4 Hz, CHO), 2.6—2.9 (5 H, m, Ph), 6.6 (1 H, dt, J 4, 7 Hz, CH_2CHCHO), 8.0—8.6 (2 H, m, CH_2*), and 8.95 (3 H, t, J 7 Hz, CH_3CH_2), *m/e* 180 (M^+, 10%), 179 (M — H, 40), 151 ($PhSCH_2CO$, 100), 123 ($PhSCH_2$, 25), and 109 (40).

2-*Methyl*-1,3-*bis*(*phenylthio*)*but*-1-*ene* (21; R^1 = H, R^2 = Ph, R^3 = R^4 = Me).—Diphenyl(phenylthiomethyl)phosphine oxide (0.7 g, 2.2 mmol) in dry THF (30 ml) and TMEDA (0.35 ml, 2.4 mmol) was treated with n-butyl-lithium (1 ml; 2.4M in hexane) at −78 °C. After 0.2 h, 3-phenylthiobutan-2-one [53] (0.4 ml, 2.4 mmol) was added and the solution was allowed to warm to room temperature during 0.5 h, giving a white precipitate and a pale yellow solution. Aqueous ammonium chloride was added, and the product extracted with chloroform (3 × 30 ml). The organic extracts were dried ($MgSO_4$) and evaporated to give an oil. Preparative t.l.c. (CH_2Cl_2) gave starting material (227 mg, 32%), and a 15 : 1 mixture of geometric isomers of the *bis*(*phenylthio*)-*olefin* (315 mg, 51% conversion, 76% yield based on starting material consumed) as an oil, R_F (CH_2Cl_2) 0.75, $\nu_{max.}$ ($CHCl_3$) 1 585 and 1 480 cm^{-1} (PhS), τ ($CDCl_3$) 2.5—3.2 (10 H, m, Ph), 4.10 and 4.20 (1 H, two m, ratio 1 : 15, CH=C), 6.12 (1 H, q, J 1 Hz, SC*H*Me), 8.10 (3 H, m, MeC=C), and 8.58 (3 H, d, J 7 Hz, CH_3CH), *m/e* 286 (M^+, 34%), 177 (M — PhS, 100), 149 ($PhSC{=}CMe$, 50), 133 ($PhSCH{=}CH$, 50), and 110 (40) (Found: M^+, 286.0857. $C_{17}H_{18}S_2$ requires M, 286.0848).

1,3-*Bis*(*phenylthio*)*pent*-1-*ene* (21; R^1 = R^4 = H, R^2 = Ph, R^3 = Et).—In a similar way, diphenylphenylthiomethylphosphine oxide (0.7 g, 2.2 mmol), n-butyl-lithium (1 ml; 2.4M in hexane), and 2-phenylthiobutanal (0.33 ml, 2.4 mmol) gave an oil, which was purified by preparative t.l.c. (CH_2Cl_2) to give starting material (263 mg, 38%), and the *bis*(*phenylthio*)-*olefin* (295 mg, 48% conversion, 76%

† This compound has been prepared by a different method and partly characterised; see ref. 15.

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yield based on starting material consumed), as an oil, R_F (CH_2Cl_2) 0.79, $\nu_{max.}$ ($CHCl_3$) 1 585 and 1 480 cm^{-1} (PhS), τ ($CDCl_3$) 2.5—3.1 (10 H, m, Ph_2), 3.8—4.3 (2 H, m, CH=CH), 6.45 (1 H, q, J 6 Hz, =CHC*H*CH_2), 8.1—8.5 (2 H, m, CH_2*CH_3), and 8.97 (3 H, t, J 8 Hz, CH_3CH_2), *m/e* 286 (M^+, 13), 177 (M — PhS, 100), 135 (20), and 109 (26) (Found: M^+, 286.0845. $C_{17}H_{18}S_2$ requires M, 286.0848).

3,5-*Bis*(*phenylthio*)*hept*-3-*ene* (21; $R^1 = R^3 = Et$, $R^2 = Ph$, $R^4 = H$).—In a similar way, diphenyl-1-(phenylthio)-propylphosphine oxide (0.35 g, 1 mmol), n-butyl-lithium (0.6 ml; 1.8M in hexane), TMEDA (0.08 ml, 1.1 mmol), and 2-phenylthiobutanal (200 mg, 1.11 mmol) gave an oil, which was purified by preparative t.l.c. (CH_2Cl_2) to give starting material (170 mg, 48%) and a 3 : 2 mixture of geometric isomers of the *bis*(*phenylthio*)-*olefin* (109 mg, 35% conversion, 68% yield based on starting material consumed), as an oil, R_F (CH_2Cl_2) 0.77, $\nu_{max.}$ (film) 1 620 (C=C), 1 580 and 1 475 cm^{-1} (PhS), τ ($CDCl_3$) 2.5—2.9 (10 H, m, PhS), 4.30 and 4.44 (1 H, two d, J 10 Hz, ratio 2 : 3, =C*H*CH), 5.56 and 6.12 (1 H, two dt, J 10, 6 Hz, =CHC*H*CH_2), 7.8—8.5 (4 H, m, $[CH_2]_2$), and 8.8—9.1 (6 H, m, Me_2), *m/e* 314 (M^+, 6%), 205 (M — PhS, 100), 163 ($PhSC_4H_6$, 40), and 110 (PhSH, 70) (Found: M^+, 314.1158. $C_{19}H_{22}S_2$ requires M, 314.1161).

3-*Methoxy*-2-*methyl*-1-*phenylthiobut*-1-*ene* (28).—Diphenyl(phenylthiomethyl)phosphine oxide (2 g, 6.2 mmol), and n-butyl-lithium (2.9 ml; 2.4M in hexane), were stirred at −78 °C in dry THF (40 ml) for 0.2 h. The orange anion was quenched with 3-methoxybutan-2-one [39] (27) (0.78 ml, 6.8 mmol), and the mixture was allowed to warm to room temperature during 0.5 h. A thick white precipitate formed, which was dissolved with aqueous ammonium chloride, and the product was extracted with chloroform (3 × 40 ml). The extract was dried ($MgSO_4$) and evaporated to give an oil. Column chromatography (CH_2Cl_2) gave the *phenylthio-methoxyallyl compound* (1.21 g, 95%) as a 1 : 1 mixture of geometric isomers, R_F (CH_2Cl_2) 0.50, $\nu_{max.}$ (film) 1 625 (C=C), 1 585, and 1 480 cm^{-1} (PhS), τ ($CDCl_3$) 2.6—2.9 (5 H, m, Ph), 3.8 and 3.9 (1 H, two q, J 1 Hz, ratio 1 : 1, C*H*=CMe), 5.50, 6.24 (1 H, two q, J 6 Hz, C*H*Me), 6.78 (3 H, s, MeO), 8.21 and 8.24 (3 H, two d, J 1 Hz, MeC=C), and 8.74 and 8.77 (3 H, two d, J 6 Hz, CH_3CH), *m/e* 208 (M^+, 45%), 193 (M — Me, 36), and 99 (M — PhS, 100) (Found: M^+, 208.0917. $C_{12}H_{16}OS$ requires M, 208.0921).

Treatment of 3-*Methoxy*-2-*methyl*-1-*phenylthiobut*-1-*ene with Benzenethiol*.—The phenylthio-methoxyallyl compound (28) (112 mg) was heated under reflux in chloroform (30 ml) with benzenethiol (0.1 ml) and toluene-*p*-sulphonic acid (35 mg) for 18 h. The solution was washed with aqueous sodium carbonate (20 ml), dried ($MgSO_4$), and evaporated. The resulting oil after preparative t.l.c. (CH_2Cl_2) gave the 1,3-bis(phenylthio)-olefin (29) (155 mg, 98%), identical with that prepared *via* 3-phenylthiobutan-2-one.

[7/830 *Received*, 12*th May*, 1977]