

Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 12.¹ Extrusion of Ph₃P from sulfonyl ylides and reactivity of the resulting sulfonyl carbenes

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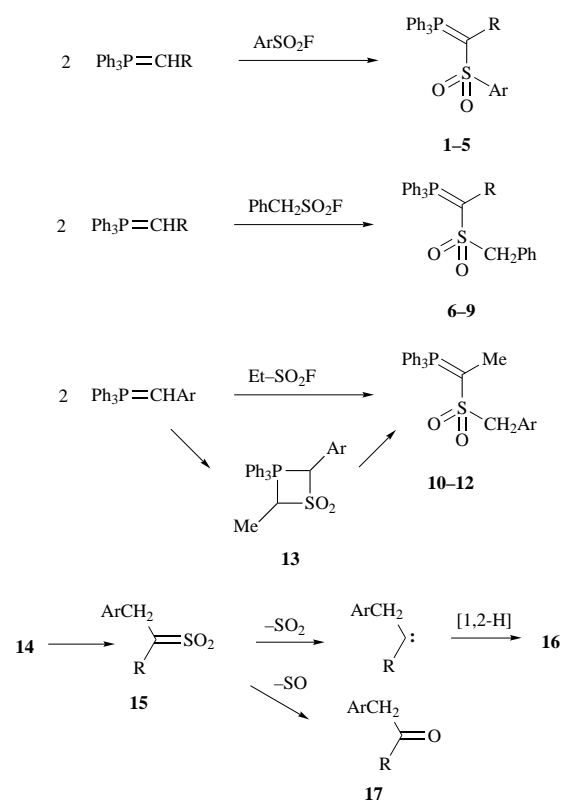
Twelve sulfonyl stabilised phosphorus ylides have been prepared and their behaviour upon flash vacuum pyrolysis at 600 °C has been examined. Examples with an arylsulfonyl substituent undergo loss of Ph₃PO to give intractable products but those with an arylmethylsulfonyl substituent separately lose Ph₃P and SO₂ to give products consistent with the intermediacy of sulfonyl carbenes. X-Ray structure determinations of one ylide from each series show a more significant P–O non-bonding interaction in the first case, providing some explanation for the different thermal reactivity.

In previous parts of this series we have shown that thermal extrusion of phosphine oxide from phosphorus ylides stabilised by an α -acyl group proceeds efficiently using flash vacuum pyrolysis (FVP) to provide access to a variety of different alkyne types. The corresponding reaction of phosphinimines stabilised by an α -acyl group to give nitriles was reported at an early date.² Although sulfonyl stabilised phosphorus ylides are well known,³ their pyrolysis has not previously been studied but it is expected to give interesting results since extrusion of Ph₃PO would give sulfonyl carbenes while SO₂ could be lost directly to afford non-stabilised ylides. We report here the synthesis of a range of sulfonyl stabilised ylides and their behaviour upon FVP which in fact leads to loss of Ph₃P and SO₂ to give products which can be explained by the intermediacy of sulfonyl carbenes.⁴

Results and discussion

As reported by van Leusen, α -sulfonyl ylides cannot be prepared by treatment of an ylide with a sulfonyl chloride since this results in formation of the α -chloro ylide.³ The problem can be resolved by first converting the sulfonyl chlorides into the corresponding sulfonyl fluorides by treatment with an excess of aqueous potassium fluoride.⁵ These then react in the desired sense³ and in this way the compounds 1–9 were obtained in moderate to good yield as shown in Table 1. Three further examples 10–12 were obtained by using ethanesulfonyl fluoride in a reaction which takes a rather unexpected course involving [2 + 2] cycloaddition between methylsulfene and the ylide to give the intermediates 13.⁶ The sulfonyl ylides were obtained as high-melting point stable solids which gave the expected analytical and spectroscopic data including ³¹P NMR signals in the range $\delta_p + 16.9$ –21.7.

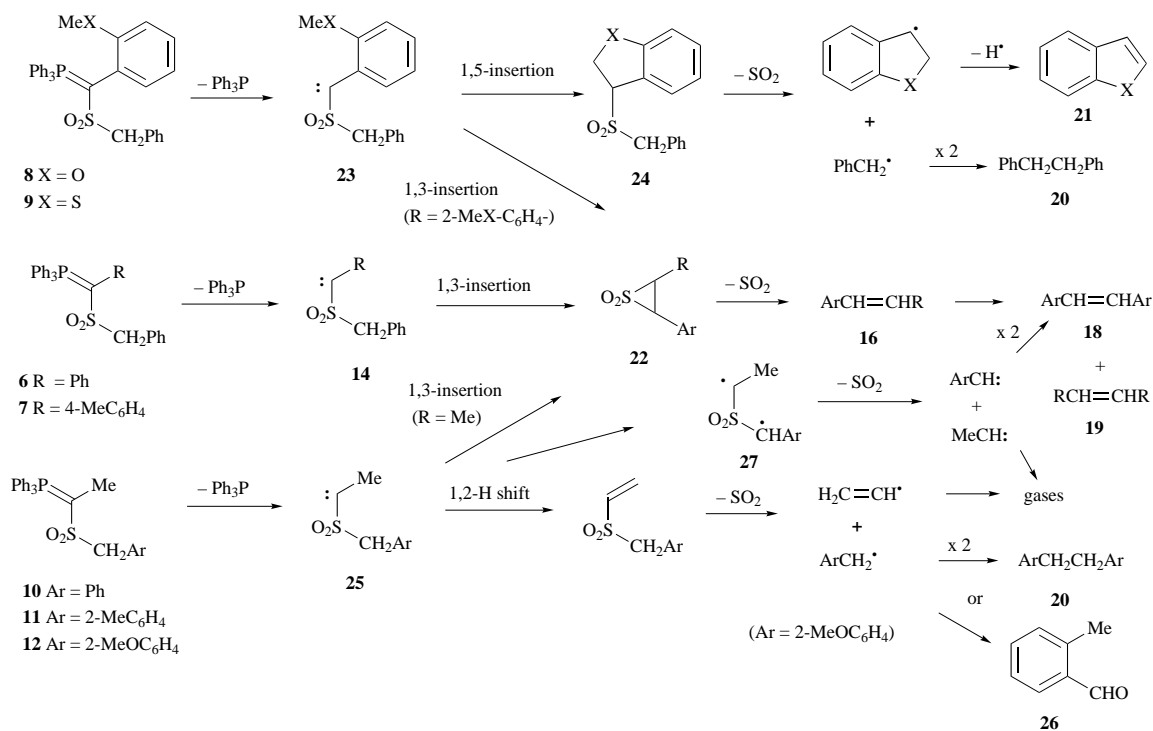
When the arylsulfonyl examples 1–5 were subjected to FVP at 600 °C and 0.01 Torr using a conventional flow system (contact time \approx 10 ms) they gave rather disappointing results. The products included Ph₃PO together with complex mixtures of sulfones and hydrocarbons, most of which could not be identified. In contrast to this, the arylmethylsulfonyl examples 6–12



underwent clean reaction at 600 °C to give well defined products. In each case a mixture of Ph₃P, Ph₃PO and Ph₃PS was produced together with the other products shown in Table 2. The phosphorus products can be accounted for by the separate extrusion of Ph₃P and SO₂ which then combine to some extent. The reaction of Ph₃P with SO₂ to give Ph₃PO and Ph₃PS, which was confirmed by a control experiment, is well known⁷ and in this case most likely occurs between the hot Ph₃P condensed at the furnace exit and SO₂ in the gas stream.

In all cases the alkenes 16 were formed and for 6 and 7 these were the main products. The formation of 16 can be explained, as shown in Scheme 1, by initial extrusion of Ph₃P to give sulfonyl carbenes 14. Intramolecular 1,3-insertion of the

[†] To receive any correspondence concerning the X-ray structure determinations.



Scheme 1

Table 1 Preparation of ylides 1–12

	R	Ar	Yield (%)	δ_p /ppm
1	Me	Ph	71	19.8
2	Et	Ph	78	20.0
3	Me	4-MeC ₆ H ₄	79	19.6
4	Et	4-MeC ₆ H ₄	26	19.8
5	Pr	4-MeC ₆ H ₄	67	19.8
6	Ph	—	82	18.2
7	4-MeC ₆ H ₄	—	72	18.1
8	2-MeOC ₆ H ₄	—	40	17.3
9	2-MeSC ₆ H ₄	—	67	16.9
10	—	Ph	62	20.8
11	—	2-MeOC ₆ H ₄	66	21.7
12	—	2-MeOC ₆ H ₄	58	20.8

carbene into benzylic CH would give the thiirane dioxide **22** which readily loses SO₂⁸ to give **16**. For **7** and **10–12** apparent metathesis of alkene **16** to give **18** and **19** was observed under the pyrolysis conditions and evidence in confirmation of this was obtained by separate pyrolysis of **16**. The yield of **18** obtained, particularly from **10–12**, seems rather high to be explained wholly by this mechanism and an alternative route to these products is provided by intramolecular hydrogen atom abstraction in carbenes **14** and **25** to afford the diradicals **27** which may fragment as shown with loss of SO₂ to produce the carbenes which dimerise to give **18**. An alternative route from **6** and **7** to **22** might involve proton transfer from the benzylic position to the ylide carbon and intramolecular attack of the resulting anion with expulsion of the phosphine. The latter process has been reported in the reaction of phosphonium ylides with sulfene to give a thiirane dioxide and Ph₃P,⁹ and also has some precedent in the chemistry of sulfonyl sulfonium and sulfoxonium ylides.¹⁰ The involvement of ionic intermediates in the gas-phase seems unlikely and, more importantly, this mechanism is not in accord with the products obtained from **8–12**. The formation of **16** could also be explained by an alternative mechanism involving rearrangement of **14** to the sulfene **15** in a process analogous to the Wolff rearrangement, followed by loss of SO₂ and a 1,2-H shift in the resulting carbene. However, while there is ample precedent for the rearrangement to **15**,¹¹ all previous pyrolyses of sulfenes¹² have resulted in

Table 2 FVP of ylides 6–12 at 600 °C

Ylide	Pyrolysis products (%)					Phosphorus products (ratio)		
	16	18	19	20	21	Ph ₃ P	Ph ₃ PO	Ph ₃ PS
6	77	—	—	—	—	9	67	24
7	47	6	9	—	—	10	60	30
8	39	—	—	11	14	25	57	18
9	5	—	—	29	58	63	28	9
10	24	7	(gas)	49	—	12	64	24
11	7	9	(gas)	34	—	12	60	28
12	6	5	(gas)	<i>a</i>	—	10	57	33

^a Product **26** formed (22%).

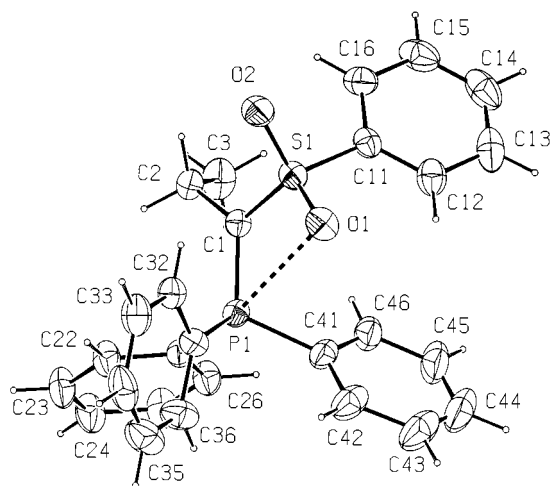
predominant loss of SO to give ketones **17** which were never detected here.

In an attempt to verify the involvement of carbenes, ylides in which the carbene would have an alternative reaction pathway open to it were examined. Thus, for ylides **8** and **9** in which R is *o*-methoxy- or *o*-methylthio-phenyl, **16** was still formed, but a new process gave rise to bibenzyl **20** together with benzofuran and benzothiophene, respectively. These products may be explained by the alternative intramolecular insertion of carbene **23** into CH of the OMe or SMe group to give **24**. A related intramolecular insertion of sulfonyl carbenes into CH to give a five-membered ring has been reported.¹³ Loss of SO₂ from this sulfone would then give two radicals, one of which aromatises by loss of an H atom to **21**, while the other dimerises to give bibenzyl. Further support for this route was provided by the GC-MS identification as minor products of 2,3-dihydrobenzofuran from **8** and 3-benzyl-2,3-dihydrobenzothiophene resulting from direct SO₂ extrusion from **24** in the case of **9**.

For the three remaining compounds **10–12**, the products **16** and **18** were formed (but-2-ene **19** was presumed to be present but was not isolated), but the major process was now the formation of benzyl radical products **20**. The presumed intermediate **25** can now undergo a 1,2-H shift to give the vinyl sulfone. Loss of SO₂ from this would give vinyl radical, which presumably leads to gaseous products, and the benzyl radical which dimerises to give **20** or, in the case of 2-methoxybenzyl-substituted **25**¹⁴ isomerises with loss of H⁺ to give *o*-tolualdehyde **26**.

Table 3 Selected bond lengths (Å) and angles (°) for **2** and **6**

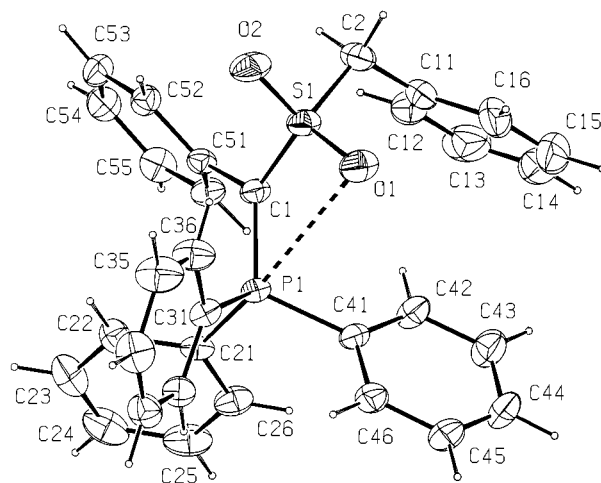
2		6	
S1–O1	1.448(2)	S1–O1	1.440(2)
S1–O2	1.448(2)	S1–O2	1.447(2)
S1–C1	1.686(2)	S1–C1	1.695(3)
S1–C11	1.779(3)	S1–C2	1.800(4)
P1–C1	1.707(2)	P1–C1	1.724(3)
P1–C21	1.817(2)	P1–C21	1.812(3)
P1–C31	1.808(3)	P1–C31	1.817(3)
P1–C41	1.812(3)	P1–C41	1.802(3)
P1–O1	2.883(2)	P1–O1	2.973(2)
O1–S1–O2	117.80(11)	O1–S1–O2	115.51(17)
O1–S1–C1	107.64(11)	O1–S1–C1	107.79(15)
O1–S1–C11	105.98(12)	O1–S1–C2	110.29(18)
O2–S1–C1	110.75(12)	O2–S1–C1	114.00(17)
O2–S1–C11	104.10(12)	O2–S1–C2	101.80(19)
C1–S1–C11	110.33(11)	C1–S1–C2	107.01(18)
C1–P1–C21	107.81(11)	C1–P1–C21	107.02(15)
C1–P1–C31	116.22(12)	C1–P1–C31	116.89(16)
C1–P1–C41	112.81(13)	C1–P1–C41	114.96(16)
C21–P1–C31	102.93(11)	C21–P1–C31	103.29(15)
C21–P1–C41	107.81(11)	C21–P1–C41	106.86(16)
C31–P1–C41	108.51(13)	C31–P1–C41	106.77(15)
S1–C1–P1	116.10(14)	S1–C1–P1	117.42(18)

**Fig. 1** A view of molecule **2** with our numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% level.

Although the extrusion of phosphines from phosphorus ylides to give carbenes is unusual, it has been proposed for alkoxy-¹⁵ and acyloxy-alkyldienetriphenylphosphoranes,¹⁶ and also more recently for a benzotriazolyl ylide.¹ In order to shed some light on the reason for the difference in behaviour between **1–5** and **6–12**, the structure of one example from each group was determined using X-ray diffraction. There have been few previous X-ray studies of sulfonyl ylides, although the structure of *p*-tolylsulfonylmethylene(triphenyl)phosphorane was reported at an early date.¹⁷ Views of molecules **2** and **6** are shown in Figs. 1 and 2 respectively. Selected dimensions are given in Table 3 and are entirely in accord with anticipated values. Of interest are the P1...O1 intramolecular non-bonded contacts in the two structures [2.883(2) Å in **2** compared with 2.973(2) Å in **6**]. The P...O distance is ≈0.1 Å shorter in **2** than in **6**, consistent with the extrusion of Ph₃PO rather than Ph₃P.

Experimental

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. Infrared spectra were recorded for solutions in chloroform in matched sodium chloride cells of path length 0.1 mm, on a Perkin-Elmer 1420 instrument. NMR spectra were obtained for ¹H at 80 MHz using a Bruker WP80

**Fig. 2** A view of molecule **6** with our numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% level.

instrument, for ¹³C at 75 MHz on a Bruker AM300 instrument, and for ³¹P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in CDCl₃ with internal Me₄Si as reference for ¹H and ¹³C and external 85% H₃PO₄ as reference for ³¹P. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants *J* are in Hz. Mass spectra were obtained on an A.E.I. MS-902 spectrometer using electron impact at 70 eV. GC–MS data were obtained using a Hewlett Packard 5890A chromatograph coupled to a Finnigan Inco mass spectrometer. Dry THF was freshly distilled from potassium benzophenone ketyl under N₂.

The required quaternary phosphonium salts were commercially available or were readily prepared by reaction of the appropriate alkyl halides with triphenylphosphine in boiling toluene. The following two salts do not appear to have been characterised before.

2-Methoxybenzyl(triphenyl)phosphonium bromide. A solution of 2-methoxybenzyl bromide¹⁸ (1 equiv.) and triphenylphosphine (1 equiv.) in toluene was heated under reflux for 18 h. The product was filtered off, washed with diethyl ether and dried to give colourless crystals (68%), mp 219–220 °C (Found: C, 67.3; H, 5.2. C₂₆H₂₄BrOP requires C, 67.4; H, 5.2%). δ_H 8.0–7.7 (15 H, m), 7.6–7.25 (2 H, m), 7.0–6.7 (2 H, m), 5.19 (2 H, d, *J* 14) and 3.30 (3 H, s); δ_C(*J*_{C–P}) 157.0 (5), 134.9 (3 C, 2), 133.9 (6 C, 10), 132.1 (6), 130.3 (4), 130.0 (6 C, 12), 120.9 (3), 117.8 (3 C, 85), 115.2 (9), 110.4 (2), 54.8 and 25.3 (49); δ_P +21.5.

2-Methylthiobenzyl(triphenyl)phosphonium chloride. Thio-salicylic acid was *S*-methylated using Me₂SO₄ (92%) and the resulting acid converted *via* the acid chloride (SOCl₂, 89%) and the methyl ester (MeOH, 95%) to 2-methylthiobenzyl alcohol (LiAlH₄, 89%). This was then chlorinated (SOCl₂, 75%) and the resulting 2-methylthiobenzyl chloride subjected to reaction as above to give the product as colourless crystals (62%), mp 230–234 °C (Found: C, 71.6; H, 5.3. C₂₆H₂₄ClPS requires C, 71.8; H, 5.6%). δ_H 7.8–7.5 (15 H, m), 7.4–7.0 (4 H, m), 5.48 (2 H, d, *J* 15) and 2.08 (3 H, s); δ_C(*J*_{C–P}) 140.0 (6), 135.0 (3 C, 2), 134.3 (6 C, 10), 131.8 (5), 130.1 (6 C, 12), 129.5 (4), 128.7 (3), 127.1 (9), 126.7 (3), 117.7 (3 C, 86), 28.7 (48) and 17.3; δ_P +22.3.

The sulfonyl fluorides were prepared by treatment of the corresponding sulfonyl chlorides with boiling aqueous potassium fluoride and were obtained as follows: benzenesulfonyl fluoride (53%), bp 62–63 °C/6 Torr (lit.,⁵ 207 °C/760 Torr); toluene-*p*-sulfonyl fluoride (90%), bp 92–93 °C/9 Torr, mp 41–42 °C (lit.,⁵ 41–42 °C); phenylmethanesulfonyl fluoride (54%), mp 89–90 °C (lit.,¹⁹ 90–91 °C); ethanesulfonyl fluoride (60%), bp 133–134 °C (lit.,¹⁹ 134–135 °C).

Preparation of the sulfonyl ylides **1–12**

A suspension of the appropriate phosphonium salt (25 mmol)

in dry THF (150 cm³) was stirred at RT under nitrogen while butyllithium in hexane (26 mmol) was added by syringe. After the addition the mixture was stirred for 30 min and then a solution of the sulfonyl fluoride (12.5 mmol) in dry THF (10 cm³) was added slowly. After 2–3 h the mixture was filtered and the filtrate was evaporated. The residue was dissolved in CH₂Cl₂ (250 cm³) and washed with water (3 × 100 cm³), dried and evaporated. The residue was triturated with diethyl ether to give the product as a yellow solid which was recrystallised from ethyl acetate–hexane.

(1-Phenylsulfonylethylidene)triphenylphosphorane 1. From ethyl(triphenyl)phosphonium bromide and benzenesulfonyl fluoride as yellow crystals (71%), mp 138–140 °C (Found: C, 72.6; H, 5.4. C₂₆H₂₃O₂PS requires C, 72.5; H, 5.4%); ν_{\max} (film)/cm⁻¹ 1582, 1480, 1435, 1300, 1270, 1220, 1180, 1110, 1068, 992, 780, 747, 720 and 690; δ_{H} 7.8–7.25 (20 H, m) and 1.72 (3 H, d, *J* 13); δ_{P} +19.8; *m/z* 430 (M⁺, 57%), 415 (2), 365 (4), 294 (9), 289 (100), 277 (36), 262 (25) and 183 (85).

(1-Phenylsulfonylprop-1-ylidene)triphenylphosphorane 2. From propyl(triphenyl)phosphonium bromide and benzenesulfonyl fluoride as yellow crystals (78%), mp 136–139 °C (Found: C, 72.9; H, 5.6. C₂₇H₂₅O₂PS requires C, 73.0; H, 5.7%); ν_{\max} /cm⁻¹ 1592, 1442, 1365, 1322, 1260, 1177, 1145, 1120, 1106, 1073, 963, 940, 758, 720, 699 and 648; δ_{H} 7.85–7.25 (20 H, m), 2.12 (2 H, d of q, *J* 19, 7) and 0.83 (3 H, t, *J* 7); δ_{C} 134.8 (2 C), 134.0 (d, *J* 10, C-2 of P-Ph), 131.7 (d, *J* 2, C-4 of P-Ph), 129.7, 127.9 (2 C), 128.4 (d, *J* 12, C-3 of P-Ph), 128.0, 126.3 (d, *J* 94, C-1 of P-Ph), 41.3 (d, *J* 123, P=C), 21.5 (d, *J* 10, CH₂) and 18.2 (CH₃); δ_{P} +20.0; *m/z* 444 (M⁺, 12%), 430 (29), 429 (100), 414 (1), 303 (10), 287 (43), 279 (2), 262 (5) and 183 (19).

[1-(4-Methylphenylsulfonyl)ethylidene]triphenylphosphorane 3. From ethyl(triphenyl)phosphonium bromide and toluene-*p*-sulfonyl fluoride as yellow crystals (79%), mp 150–153 °C (Found: C, 73.0; H, 5.7. C₂₇H₂₅O₂PS requires C, 73.0; H, 5.7%); ν_{\max} /cm⁻¹ 1595, 1440, 1315, 1260, 1186, 1142, 1105, 1070, 1002, 905, 865, 825, 756, 721, 699 and 670; δ_{H} 7.8–7.2 (17 H, m), 7.05 (2 H, half AB pattern, *J* 9), 2.35 (3 H, s) and 1.69 (3 H, d, *J* 13); δ_{P} +19.6; *m/z* 444 (M⁺, 33%), 379 (7), 294 (16), 289 (100), 282 (22), 277 (56), 262 (22) and 183 (82).

[1-(4-Methylphenylsulfonyl)prop-1-ylidene]triphenylphosphorane 4. From propyl(triphenyl)phosphonium bromide and toluene-*p*-sulfonyl fluoride as yellow crystals (26%), mp 161–163 °C (Found: C, 73.0; H, 6.15. C₂₈H₂₇O₂PS requires C, 73.3; H, 5.9%); ν_{\max} /cm⁻¹ 1586, 1435, 1310, 1280, 1254, 1165, 1133, 1104, 1062, 968, 950, 927, 810, 752, 740, 712, 690 and 660; δ_{H} 7.85–7.3 (15 H, m), 7.27 and 7.03 (4 H, AB pattern, *J* 9), 2.33 (3 H, s), 2.3–1.8 (2 H, m) and 0.82 (3 H, t, *J* 7); δ_{P} +19.8; *m/z* 458 (M⁺, 56%), 443 (100), 423 (8), 409 (20), 391 (3), 377 (2), 363 (3), 328 (3), 310 (49), 294 (100), 284 (17) and 269 (26).

[1-(4-Methylphenylsulfonyl)but-1-ylidene]triphenylphosphorane 5. From butyl(triphenyl)phosphonium bromide and toluene-*p*-sulfonyl fluoride as yellow crystals (67%), mp 184–186 °C (Found: C, 73.5; H, 6.2. C₂₉H₂₉O₂PS requires C, 73.7; H, 6.2%); ν_{\max} /cm⁻¹ 1586, 1440, 1256, 1218, 1186, 1140, 1110, 1065, 1030, 1010, 962, 832, 812, 750, 718 and 687; δ_{H} 7.95–7.25 (15 H, m), 7.37 and 7.10 (4 H, AB pattern, *J* 9), 2.37 (3 H, s), 2.0–1.1 (4 H, m) and 0.55 (3 H, t, *J* 7); δ_{P} +19.8; *m/z* 472 (M⁺, 11%), 443 (100), 423 (25), 317 (6), 287 (81) and 262 (13).

[(Phenylmethylsulfonyl)(phenyl)methylene]triphenylphosphorane 6. From benzyl(triphenyl)phosphonium chloride and phenylmethanesulfonyl fluoride as pale yellow crystals (82%), mp 210–211 °C (lit.,⁶ 210–211 °C) (Found: C, 75.9; H, 5.1. C₃₃H₂₇O₂PS requires C, 75.9; H, 5.4%); δ_{H} 7.55–6.95 (25 H, m) and 3.98 (2 H, s); δ_{C} 135.5 (2 C, d, *J* 3, C-2 of P=C-Ph), 134.8 (d, *J* 9, C-1 of P=C-Ph), 133.8 (d, *J* 10, C-2 of P-Ph), 131.5 (d, *J* <2, C-4 of P-Ph), 131.4, 131.2 (2 C), 128.3 (d, *J* 12, C-3 of P-Ph), 128.1 (2 C), 127.7 (2 C), 127.5, 126.2 (d, *J* 119, C-1 of P-Ph), 61.4 (CH₂) and 47.0 (d, *J* 130, P=C) (one 4ry carbon not apparent); δ_{P} +18.2; *m/z* 506 (M⁺, 18%), 415 (55), 367 (32), 351 (58), 273 (8), 271 (7), 241 (14), 183 (28), 165 (67) and 105 (100).

[(4-Methylphenyl)(phenylmethylsulfonyl)methylene]triphenylphosphorane 7. From 4-methylbenzyl(triphenyl)phosphonium bromide and phenylmethanesulfonyl fluoride as pale yellow crystals (72%), mp 188–189 °C (Found: C, 75.8; H, 5.8. C₃₃H₂₉O₂PS requires C, 76.1; H, 5.6%); ν_{\max} /cm⁻¹ 1625, 1502, 1483, 1435, 1264, 1244, 1144, 1106, 1094, 1043, 1028, 935, 864, 788, 754, 714 and 694; δ_{H} 7.55–6.95 (22 H, m), 6.84 (2 H, half AB pattern, *J* 6), 3.97 (2 H, s) and 2.21 (3 H, s); δ_{P} +18.1; *m/z* 520 (M⁺, 15%), 429 (36), 414 (10), 381 (32), 366 (100), 352 (14), 277 (60) and 119 (55).

[(2-Methoxyphenyl)(phenylmethylsulfonyl)methylene]triphenylphosphorane 8. From 2-methoxybenzyl(triphenyl)phosphonium bromide and phenylmethanesulfonyl fluoride as colourless crystals (40%), mp 210–213 °C (Found: C, 73.6; H, 5.4. C₃₃H₂₉O₃PS requires C, 73.9; H, 5.4%); ν_{\max} /cm⁻¹ 1590, 1486, 1440, 1312, 1265, 1192, 1122, 1103, 1044, 1028, 1000, 965, 756, 723 and 698; δ_{H} 7.95–6.8 (23 H, m), 6.50 (1 H, m), 4.03 (2 H, s) and 3.35 (3 H, s); δ_{P} +17.3; *m/z* 536 (M⁺, 90%), 445 (100), 415 (78), 397 (22), 381 (32), 367 (30), 351 (48), 277 (40) and 262 (90).

[(2-Methylthiophenyl)(phenylmethylsulfonyl)methylene]triphenylphosphorane 9. From 2-methylthiobenzyl(triphenyl)phosphonium chloride and phenylmethanesulfonyl fluoride as colourless crystals (67%), mp 248–251 °C (Found: C, 71.3; H, 5.0. C₃₃H₂₉O₂PS₂ requires C, 71.7; H, 5.3%); ν_{\max} /cm⁻¹ 1439, 1265, 1105, 1080, 1040, 1028, 950, 938, 772, 754, 735, 720 and 703; δ_{H} 8.0–7.1 (23 H, m), 6.91 (1 H, m), 4.26 (2 H, s) and 2.15 (3 H, s); δ_{P} +16.9; *m/z* 552 (M⁺, 36%), 461 (40), 397 (16), 350 (18), 277 (90), 262 (100), 219 (24) and 137 (50).

(1-Phenylmethylsulfonylethylidene)triphenylphosphorane 10. From benzyl(triphenyl)phosphonium chloride and ethanesulfonyl fluoride as yellow crystals (62%), mp 170–172 °C (lit.,⁶ 171.5–172.5 °C); δ_{H} 7.7–7.4 (15 H, m), 7.27 (5 H, s), 3.97 (2 H, s) and 1.58 (3 H, d, *J* 14); δ_{P} +20.8.

[1-(2-Methylphenylmethylsulfonyl)ethylidene]triphenylphosphorane 11. From 2-methylbenzyl(triphenyl)phosphonium chloride and ethanesulfonyl fluoride as colourless crystals (66%), mp 150–153 °C (Found: M⁺, 458.1461. C₂₈H₂₇O₂PS requires M⁺, 458.1469); ν_{\max} /cm⁻¹ 1588, 1440, 1318, 1298, 1264, 1150, 1139, 1112, 1056, 998, 842, 765, 752, 725 and 693; δ_{H} 7.9–7.4 (15 H, m), 7.3–7.1 (4 H, m), 4.34 (2 H, br s), 2.26 (3 H, s) and 1.74 (3 H, d, *J* 15); δ_{P} +21.7; *m/z* 458 (M⁺, 18%), 354 (22), 353 (100), 305 (16), 291 (52), 289 (77), 263 (47) and 183 (48).

[1-(2-Methoxyphenylmethylsulfonyl)ethylidene]triphenylphosphorane 12. From 2-methoxybenzyl(triphenyl)phosphonium chloride and ethanesulfonyl fluoride as colourless crystals (58%), mp 193–194 °C (Found: C, 70.75; H, 5.9. C₂₈H₂₇O₃PS requires C, 70.9; H, 5.7%); ν_{\max} /cm⁻¹ 1580, 1493, 1436, 1264, 1250, 1235, 1188, 1130, 1100, 1072, 1022, 892, 872, 787, 756, 712 and 694; δ_{H} 7.8–7.35 (15 H, m), 7.25 (2 H, m), 7.0–6.75 (2 H, m), 4.30 (2 H, s), 3.78 (3 H, s) and 1.62 (3 H, d, *J* 16); δ_{P} +20.8; *m/z* 474 (M⁺, 12%), 353 (100), 305 (4), 289 (12), 277 (8), 262 (56), 205 (24) and 121 (18).

Flash vacuum pyrolysis of ylides

The apparatus used was as described previously.²⁰ All pyrolyses were conducted at pressures in the range 10⁻³ to 10⁻¹ Torr and were complete within 1 h. Under these conditions the contact time in the hot zone was estimated to be ≈10 ms.

In some cases the phosphorus containing products collected at the furnace exit and the more volatile products were recovered from the cold trap. Where necessary in the case of less volatile products the entire pyrolysate was washed out together and separated by chromatography. Yields were determined by calibration of the ¹H NMR spectra by adding an accurately weighed quantity of a solvent such as CH₂Cl₂ and comparing integrals, a procedure estimated to be accurate to ±10%.

FVP of the ylide **3** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist mainly of Ph₃PO together with some unreacted starting material. In the cold trap was a mixture of

Table 4 Summary of crystal data, data collection, structure solution and refinement details

(a) Crystal data		
Molecular formula	C ₂₇ H ₂₅ O ₂ PS	C ₃₂ H ₂₇ O ₂ PS
Molar mass	444.50	506.57
Colour, habit	Colourless, plate	Colourless, block
Crystal size, mm	0.37 × 0.25 × 0.13	0.33 × 0.25 × 0.25
Crystal system	Monoclinic	Monoclinic
<i>a</i> /Å	9.1270(10)	9.0145(15)
<i>b</i> /Å	21.934(3)	9.8195(15)
<i>c</i> /Å	11.692(2)	15.018(3)
<i>a</i> (°)	90	90
<i>β</i> (°)	93.940(10)	103.320(15)
<i>γ</i> (°)	90	90
<i>V</i> /Å ³	2335.1(6)	1293.6(4)
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁
<i>Z</i>	4	2
<i>F</i> (000)	936	532
<i>d</i> _{calc}	1.264	1.300
<i>μ</i> /mm ⁻¹	0.228	0.215
(b) Data acquisition ^a		
Temp./K	294(1)	294(1)
Unit cell reflections (<i>θ</i> range°)	25 (10.0, 16.8)	25 (10.1, 18.2)
Max. <i>θ</i> (°) for reflections	26.89	26.95
<i>hkl</i> range of reflections	−11 11; 0 27; 0 14	0 11; 0 12; −19 19
Variation in 3 standard reflections	1.0	1.0
Reflexns measured	5371	3175
Unique reflections	5069	2998
<i>R</i> _{int}	0.017	0.006
Reflections with <i>I</i> > 2σ(<i>I</i>)	2449	2191
(c) Structure solution and refinement		
H-atom treatment	Riding	Riding
No. of variables in L.S.	280	325
Weights		
<i>k</i> in <i>w</i> = 1/(σ ² <i>F</i> _o ² + <i>k</i>)	(0.0640 <i>P</i>) ²	(0.0613 <i>P</i>) ²
[<i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3] <i>R</i> , <i>R</i> _w , <i>gof</i>	0.043, 0.124, 0.92	0.036, 0.099, 1.02
Flack parameter	—	−0.01(10)
Density range in final Δ map/e Å ⁻³	−0.212, 0.228	−0.228, 0.207
Final shift/error ratio	0.000	0.000

^a Data collection on an Enraf Nonius CAD4 diffractometer with graphite monochromated Mo-Kα radiation (λ 0.7107 Å).

products whose main constituents were identified by NMR spectroscopy, GC–MS and comparison with authentic samples as 4-methylphenyl vinyl sulfone; *m/z* 182 (M⁺, 12%), 139 (70), 107 (17) and 91 (100), ethyl 4-methylphenyl sulfone; δ_H 7.63 and 7.18 (4 H, AB pattern, *J* 8), 2.98 (2 H, q, *J* 7), 2.36 (3 H, s) and 1.18 (3 H, t, *J* 7); *m/z* 184 (M⁺, 9%), 155 (12), 139 (6), 108 (12), 107 (12) and 91 (100); and di(4-methylphenyl) disulfide; *m/z* 246 (M⁺, 35%), 137 (37), 123 (100) and 119 (38).

FVP of the ylide **4** (200 mg) at 750 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist almost entirely of Ph₃PO. In the cold trap was a mixture of products whose main constituents were identified by NMR spectroscopy, GC–MS and comparison with authentic samples as toluene and 4-methylphenyl prop-1-enyl sulfone; δ_H 7.7–7.3 (4 H, m), 6.91 (1 H, d of q, *J* 15, 7), 6.30 (1 H, d of q, *J* 15, 1) and 1.87 (3 H, dd, *J* 7, 1); *m/z* 196 (M⁺, 16%), 139 (100), 117 (10), 108 (25) and 91 (76).

FVP of the ylide **6** (1.0 g) at 750 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist of (*E*)-stilbene (56%), (*Z*)-stilbene (11%) and Ph₃P, Ph₃PO and Ph₃PS in a ratio of 9:67:24. Chromatography on silica using CH₂Cl₂ gave pure (*E*)-stilbene, identical with an authentic sample.

FVP of the ylide **7** (2.0 g) at 600 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist of stilbene (6%, *E*:*Z* 5:1), 4-methylstilbene (47%, *E*:*Z* 3:1), 4,4'-dimethylstilbene (9%, *E*:*Z* 2:1), bibenzyl (4%), 4-methylbibenzyl (8%), 4,4'-dimethylbibenzyl (3%) and Ph₃P, Ph₃PO and Ph₃PS in a ratio of 10:60:30. Chromatography on

silica using CH₂Cl₂ gave pure (*E*)-4-methylstilbene, identical with an authentic sample.

FVP of the ylide **8** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist of Ph₃P, Ph₃PO and Ph₃PS in a ratio of 25:57:18. In the cold trap was a mixture of products whose main constituents were identified by NMR spectroscopy, GC–MS and comparison with authentic samples as benzofuran (14%); *m/z* 118 (M⁺, 100%) 90 (65), 89 (70) and 63 (38), 2,3-dihydrobenzofuran (7%); *m/z* 120 (M⁺, 91%), 119 (67), 92 (55), 91 (100) and 65 (37), 2-methoxystilbene (39%, *E*:*Z* 5:1); δ_H 7.7–6.8 (11 H, m), 3.90 (3 H, s, *E*) and 3.82 (3 H, s, *Z*); *m/z* 210 (M⁺, 65%), 179 (18), 167 (48), 165 (26), 152 (52), 119 (64), 104 (62) and 91 (100) and bibenzyl (11%); δ_H 7.7–7.3 (10 H, m) and 2.95 (4 H, s); *m/z* 182 (M⁺, 14%), 165 (3), 104 (3) and 91 (100).

FVP of the ylide **9** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist of Ph₃P, Ph₃PO and Ph₃PS in a ratio of 63:28:9. In the cold trap was a mixture of products whose main constituents were identified by NMR spectroscopy, GC–MS and comparison with authentic samples as benzothiophene (58%); δ_H 8.1–7.9 (2 H, m) and 7.6–7.3 (4 H, m); *m/z* 134 (M⁺, 100%) 108 (6), 90 (10) and 89 (8), (*E*)-2-methylthiostilbene (5%); δ_H 7.7–7.0 (11 H, m), 2.48 (3 H, s); *m/z* 226 (M⁺, 67%), 211 (100), 178 (43), 165 (18), 151 (12) and 77 (21), 3-benzyl-2,3-dihydrobenzothiophene (5%); *m/z* 226 (M⁺, 8%), 135 (100), 134 (35) and 91 (40), and bibenzyl (29%); δ_H 7.7–7.3 (10 H, m) and 2.96 (4 H, s); *m/z* 182 (M⁺, 8%), 165 (2), 104 (3) and 91 (100).

FVP of the ylide **10** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist of Ph₃P, Ph₃PO and Ph₃PS in a ratio of 12:64:24. In the cold trap was a mixture of hydrocarbons identified by NMR spectroscopy, GC–MS and comparison with authentic samples as prop-1-enylbenzene (24%, *E:Z* 3:1), (*E*)-stilbene (7%) and bibenzyl (49%).

FVP of the ylide **11** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist of Ph₃P, Ph₃PO and Ph₃PS in a ratio of 12:60:28. In the cold trap was a mixture of products whose main constituents were identified by NMR spectroscopy, GC–MS and comparison with authentic samples as 2-methylprop-1-enylbenzene (7%, *E:Z* 1:1), 2,2'-dimethylstilbene (9%, *E:Z* 1:1) and 2,2'-dimethylbibenzyl (34%).

FVP of the ylide **12** (200 mg) at 600 °C gave an oil at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to consist of Ph₃P, Ph₃PO and Ph₃PS in a ratio of 10:57:33. In the cold trap was a mixture of products whose main constituents were identified by NMR spectroscopy, GC–MS and comparison with authentic samples as 2-methoxyprop-1-enylbenzene (6%, *E:Z* 1:1), 2,2'-dimethoxystilbene (5%, *E:Z* 1:1) and 2-methylbenzaldehyde (22%).

Authentic samples of 4,4'-dimethylstilbene, 2,2'-dimethylstilbene, 2-methoxyprop-1-enylbenzene, 2,2'-dimethoxystilbene, 2-methylprop-1-enylbenzene and prop-1-enylbenzene were prepared as mixtures of *E* and *Z* isomers by Wittig reaction under standard conditions followed by distillation or column chromatography.

FVP of 4-methylstilbene (500 mg, *E:Z* 4:1) at 750 °C gave a mixture of products which was largely unchanged starting material but was shown by ¹H NMR spectroscopy and GC–MS to also contain (*E*)-stilbene and 4,4'-dimethylstilbene (~5% of each).

FVP of prop-1-enylbenzene (500 mg) at 750 °C gave a liquid in the cold trap which was mainly the unchanged starting material and a solid at the furnace exit which was shown by GC–MS to contain (*E*)-stilbene, bibenzyl and biphenyl, all in low yield.

FVP of triphenylphosphine (100 mg) at 750 °C under a stream of SO₂ gas gave a solid at the furnace exit which was shown by ³¹P NMR spectroscopy and GC–MS to contain mainly Ph₃P together with Ph₃PO and Ph₃PS in an approximate ratio of 5:2:1.

X-Ray structure determinations

Details of crystal data, data collection, structure solution and refinement for **2** and **6** are summarised in Table 4. Molecule **6** crystallises in a chiral space group and the refinement allows the direction of the chiral axis to be determined. Structure solution was *via* the NRCVAX²¹ and SHELXS97²² programs; refinement employed all *F*² data and SHELXL97.²³ In the final refinement cycles, all non-H atoms were allowed anisotropic displacement parameters. The ORTEP²⁴ plots (Figs. 1 and 2) were prepared with the aid of PLATON.²⁵

Atomic coordinates, molecular dimensions and anisotropic displacement parameters have been deposited in CIF format at the Cambridge Crystallographic Data Centre (CCDC). For

details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans 1*, available *via* the RSC Web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/180.

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