Flash vacuum pyrolysis of stabilised phosphorus ylides. Part 12.[1] Extrusion of Ph_3P from sulfonyl ylides and reactivity of the resulting sulfonyl carbenes

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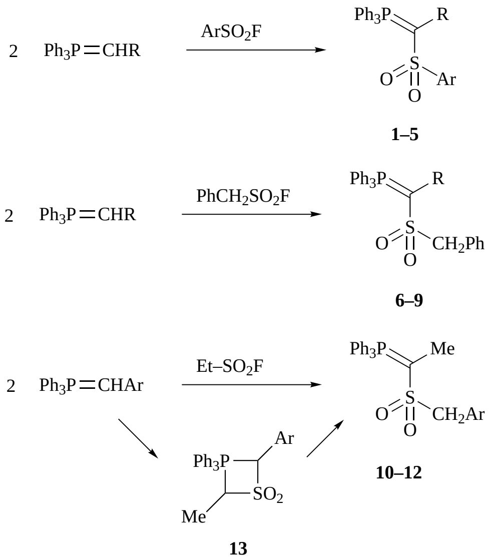
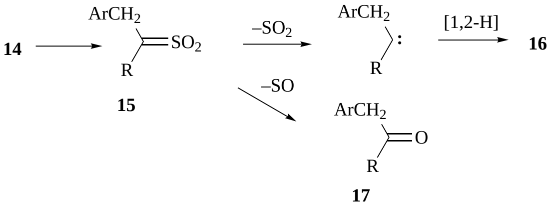
Twelve sulfonyl stabilised phosphorus ylides have been prepared and their behaviour upon flash vacuum pyrolysis at 600 °C has been examined. Examples with an arylsulfonyl substituent undergo loss of Ph_3PO to give intractable products but those with an arylmethylsulfonyl substituent separately lose Ph_3P and SO_2 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 Ph_3PO would give sulfinyl carbenes while SO_2 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 Ph_3P and SO_2 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 sense[3] 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 ^{31}P NMR signals in the range δ_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 ≈ 10 ms) they gave rather disappointing results. The products included Ph_3PO 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 Ph_3P, Ph_3PO and Ph_3PS was produced together with the other products shown in Table 2. The phosphorus products can be accounted for by the separate extrusion of Ph_3P and SO_2 which then combine to some extent. The reaction of Ph_3P with SO_2 to give Ph_3PO and Ph_3PS, which was confirmed by a control experiment, is well known[7] and in this case most likely occurs between the hot Ph_3P condensed at the furnace exit and SO_2 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 Ph_3P to give sulfonyl carbenes **14**. Intramolecular 1,3-insertion of the

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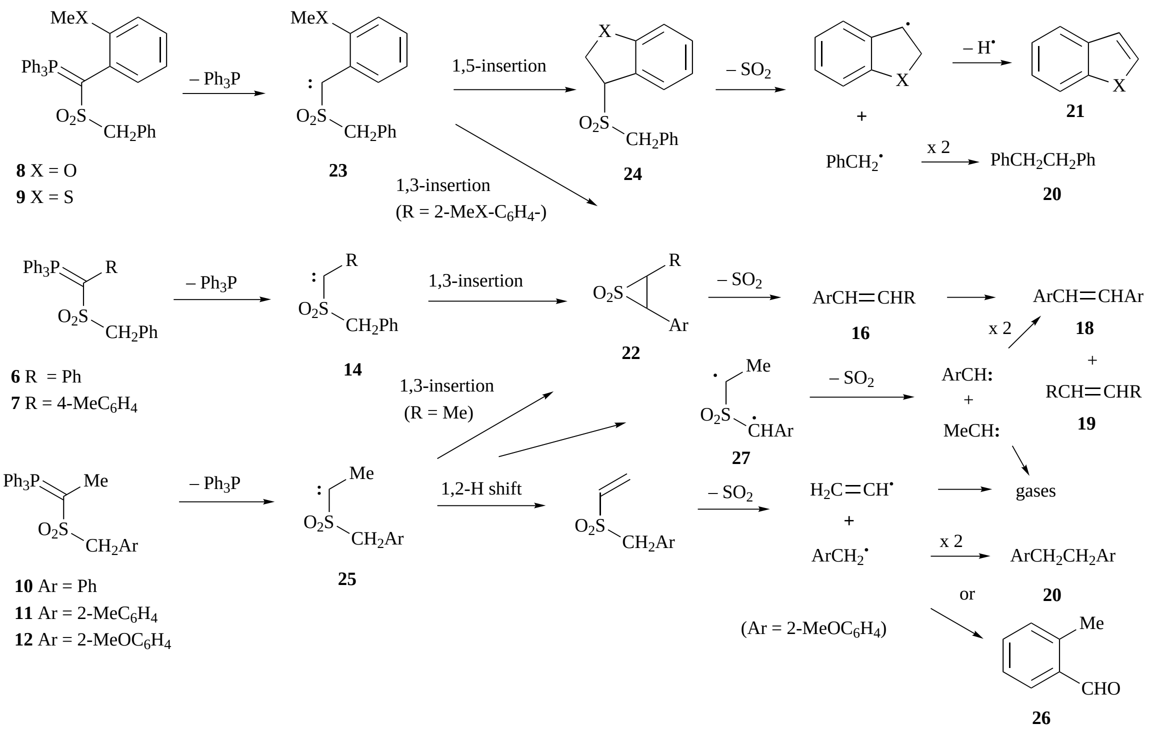
† To receive any correspondence concerning the X-ray structure determinations.



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_6H_4	79	19.6
4	Et	4-MeC_6H_4	26	19.8
5	Pr	4-MeC_6H_4	67	19.8
6	Ph	—	82	18.2
7	4-MeC_6H_4	—	72	18.1
8	2-$MeOC_6H_4$	—	40	17.3
9	2-$MeSC_6H_4$	—	67	16.9
10	—	Ph	62	20.8
11	—	2-$MeOC_6H_4$	66	21.7
12	—	2-$MeOC_6H_4$	58	20.8

Table 2 FVP of ylides **6–12** at 600 °C

	Pyrolysis products (%)					Phosphorus products (ratio)		
Ylide	**16**	**18**	**19**	**20**	**21**	Ph_3P	Ph_3PO	Ph_3PS
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)	*a*	—	10	57	33

[a] Product **26** formed (22%).

carbene into benzylic CH would give the thiirane dioxide **22** which readily loses SO_2[8] 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 SO_2 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 Ph_3P,[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 SO_2 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 sulfenes[12] have resulted in 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 SO_2 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 SO_2 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 SO_2 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)

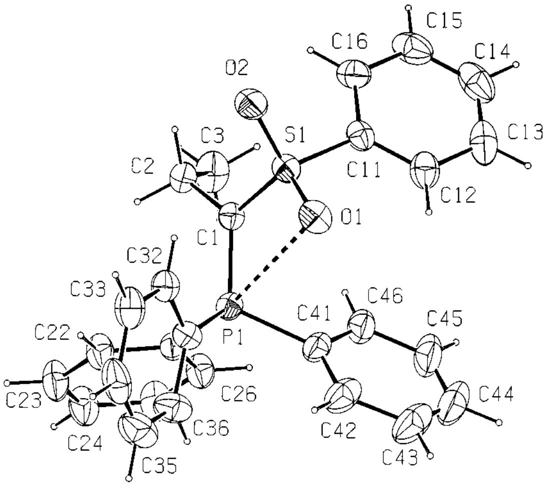


Fig. 1 A view of molecule **2** with our numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% level.

Although the extrusion of phosphines from phosphorus ylides to give carbenes is unusual, it has been proposed for alkoxy-[15] and acyloxy-alkylidenetriphenylphosphoranes,[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 Ph_3PO rather than Ph_3P.

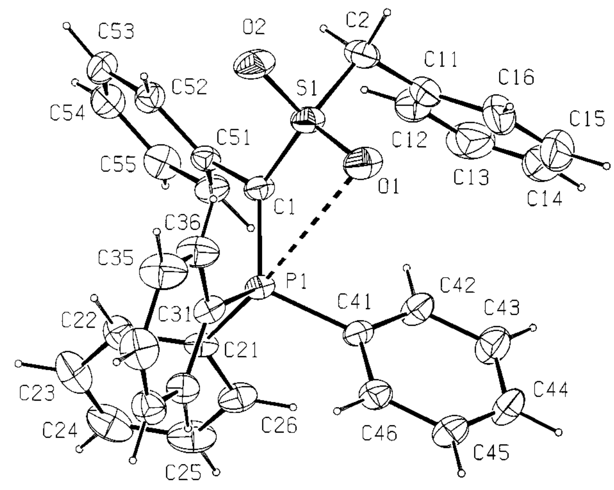


Fig. 2 A view of molecule **6** with our numbering scheme. Anisotropic displacement ellipsoids are drawn at the 30% level.

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 instrument, for ^{13}C at 75 MHz on a Bruker AM300 instrument, and for ^{31}P at 32 MHz using a Varian CFT 20 instrument. All spectra were run on solutions in $CDCl_3$ with internal Me_4Si as reference for ^1H and ^{13}C and external 85% H_3PO_4 as reference for ^{31}P. 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 Incos mass spectrometer. Dry THF was freshly distilled from potassium benzophenone ketyl under N_2.

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 bromide[18] (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. $C_{26}H_{24}BrOP$ 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); $\delta_C(J_{C-P})$ 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. Thiosalicylic acid was *S*-methylated using Me_2SO_4 (92%) and the resulting acid converted *via* the acid chloride ($SOCl_2$, 89%) and the methyl ester (MeOH, 95%) to 2-methylthiobenzyl alcohol ($LiAlH_4$, 89%). This was then chlorinated ($SOCl_2$, 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. $C_{26}H_{24}ClPS$ 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); $\delta_C(J_{C-P})$ 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 cm^3) 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 cm^3) was added slowly. After 2–3 h the mixture was filtered and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 (250 cm^3) and washed with water (3 × 100 cm^3), 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. $C_{26}H_{23}O_2PS$ 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. $C_{27}H_{25}O_2PS$ 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, CH_2) and 18.2 (CH_3); 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. $C_{27}H_{25}O_2PS$ 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. $C_{28}H_{27}O_2PS$ 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. $C_{29}H_{29}O_2PS$ 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. $C_{32}H_{27}O_2PS$ 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 (CH_2) 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. $C_{33}H_{29}O_2PS$ 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. $C_{33}H_{29}O_3PS$ 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. $C_{33}H_{29}O_2PS_2$ 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. $C_{28}H_{27}O_2PS$ 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. $C_{28}H_{27}O_3PS$ 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 ^{1}H NMR spectra by adding an accurately weighed quantity of a solvent such as CH_2Cl_2 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 ^{31}P NMR spectroscopy and GC–MS to consist mainly of Ph_3PO 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	$C_{27}H_{25}O_2PS$	$C_{32}H_{27}O_2PS$
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
a/Å	9.1270(10)	9.0145(15)
b/Å	21.934(3)	9.8195(15)
c/Å	11.692(2)	15.018(3)
α(°)	90	90
β(°)	93.940(10)	103.320(15)
γ(°)	90	90
V/Å^3	2335.1(6)	1293.6(4)
Space group	$P2_1/n$	$P2_1$
Z	4	2
F(000)	936	532
d_{calc}	1.264	1.300
μ/mm^{-1}	0.228	0.215
(b) Data aquisition[a]		
Temp./K	294(1)	294(1)
Unit cell reflections (θ range°)	25 (10.0, 16.8)	25 (10.1, 18.2)
Max. θ (°) for reflections	26.89	26.95
hkl range of reflections	−11 11; 0 27; 0 14	0 11; 0 12; −19 19
Variation in 3 standard reflections	1.0	1.0
Reflcns measured	5371	3175
Unique reflections	5069	2998
R_{int}	0.017	0.006
Reflections with $I > 2\sigma(I)$	2449	2191
(c) Structure solution and refinement		
H-atom treatment	Riding	Riding
No. of variables in L.S.	280	325
Weights		
k in $w = 1/(\sigma^2 F_o^2 + k)$	$(0.0640P)^2$	$(0.0613P)^2$
$[P = (F_o^2 + 2F_c^2)/3]$ R, R_w, gof	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 ^{31}P NMR spectroscopy and GC–MS to consist almost entirely of Ph_3PO. 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 ^{31}P NMR spectroscopy and GC–MS to consist of (E)-stilbene (56%), (Z)-stilbene (11%) and Ph_3P, Ph_3PO and Ph_3PS in a ratio of 9:67:24. Chromatography on silica using CH_2Cl_2 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 ^{31}P 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 Ph_3P, Ph_3PO and Ph_3PS in a ratio of 10:60:30. Chromatography on silica using CH_2Cl_2 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 ^{31}P NMR spectroscopy and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS 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 ^{31}P NMR spectroscopy and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS 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 ^{31}P NMR spectroscopy and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS 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 ^{31}P NMR spectroscopy and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS 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 ^{31}P NMR spectroscopy and GC–MS to consist of Ph_3P, Ph_3PO and Ph_3PS 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 ^{1}H 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 SO_2 gas gave a solid at the furnace exit which was shown by ^{31}P NMR spectroscopy and GC–MS to contain mainly Ph_3P together with Ph_3PO and Ph_3PS 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 NRCVAX[21] and SHELXS97[22] 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 ORTEP[24] 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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