Flash Vacuum Pyrolysis of Sulphonyl Stabilised Phosphorus Ylides: Generation and Reactivity of Sulphonyl Carbenes

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Thermal decomposition of arylmethylsulphonylalkylidenetriphenylphosphoranes results in loss of Ph_3P and SO_2 to give alkenes and in some cases products derived from benzylic radicals, the products are explained by a mechanism involving sulphonyl carbenes.

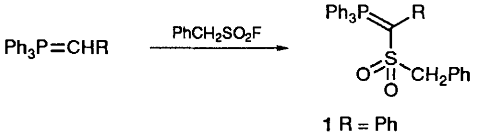
Both phosphorus ylides and phosphinimines stabilised by an α-acyl group are well known to undergo thermal extrusion of phosphine oxide to give alkynes[1] and nitriles[2] respectively. Although sulphonyl stabilised phosphorus ylides are well known[3] their pyrolysis has not previously been studied. We report here the flash vacuum pyrolysis (FVP) of a range of sulphonyl stabilised ylides to give products resulting from loss of Ph_3P and SO_2 which can be explained by the intermediacy of sulphonyl carbenes.

The required ylides† were readily prepared either by treatment of the appropriate benzylidenetriphenylphosphorane (2 equiv.) with phenylmethanesulphonyl fluoride[3] to give **1**–**4** or, using the rearrangement reported by Van Leusen,[4] with ethanesulphonyl fluoride to give **5**–**7**.

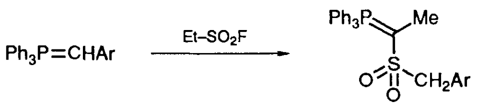
When these were subjected to FVP at 600 °C and 0.01 Torr using a conventional flow system (contact time $\approx$ 10 ms) they gave a mixture of Ph_3P, Ph_3PO and Ph_3PS together with the products shown in Table 1. The phosphorus products can be accounted for by the separate extrusion of Ph_3P and SO_2 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[5] 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 **9** were formed and for **1** and **2** these were the main products. The formation of **9** can be explained as shown in Scheme 1 by initial extrusion of Ph_3P to give sulphonylcarbenes **8**. Intramolecular 1,3-insertion of the carbene into benzylic CH would give the thiirane dioxide **14** which readily loses SO_2 to give **9**. For **2**, **5**, **6** and **7** some metathesis of alkene **9** to give **10** and **11** was observed under the pyrolysis conditions and this was confirmed by separate pyrolysis of **9**. The formation of **9** could also be explained by an alternative mechanism involving rearrangement of **8** to sulphene **15** in a process analogous to the Wolff rearrangement, followed by loss of SO_2 and 1,2-H shift in the resulting carbene. However, while there is ample precedent for the rearrangement to **15**,[6] all previous pyrolyses of sulphenes[7] have resulted in predominant loss of SO to give ketones **16** which were never detected here.

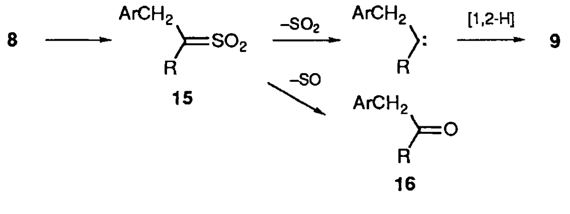
For ylides **3** and **4** in which R is *o*-methoxy- or *o*-methylthiophenyl, **9** was still formed, but a new process gave rise to bibenzyl together with benzofuran and benzothiophene respectively. These products may be explained by the alternative intramolecular insertion of carbene **17** into CH of the OMe or SMe group to give **18**. A related intramolecular insertion of sulphonyl carbenes into CH to give a five-membered ring has recently been reported.[8] Loss of SO_2 from this sulphone would then give two radicals, one of which



1 R = Ph
2 R = *p*-MeC_6H_4
3 R = *o*-$MeOC_6H_4$
4 R = *o*-$MeSC_6H_4$



5 Ar = Ph
6 Ar = *o*-MeC_6H_4
7 Ar = *o*-$MeOC_6H_4$



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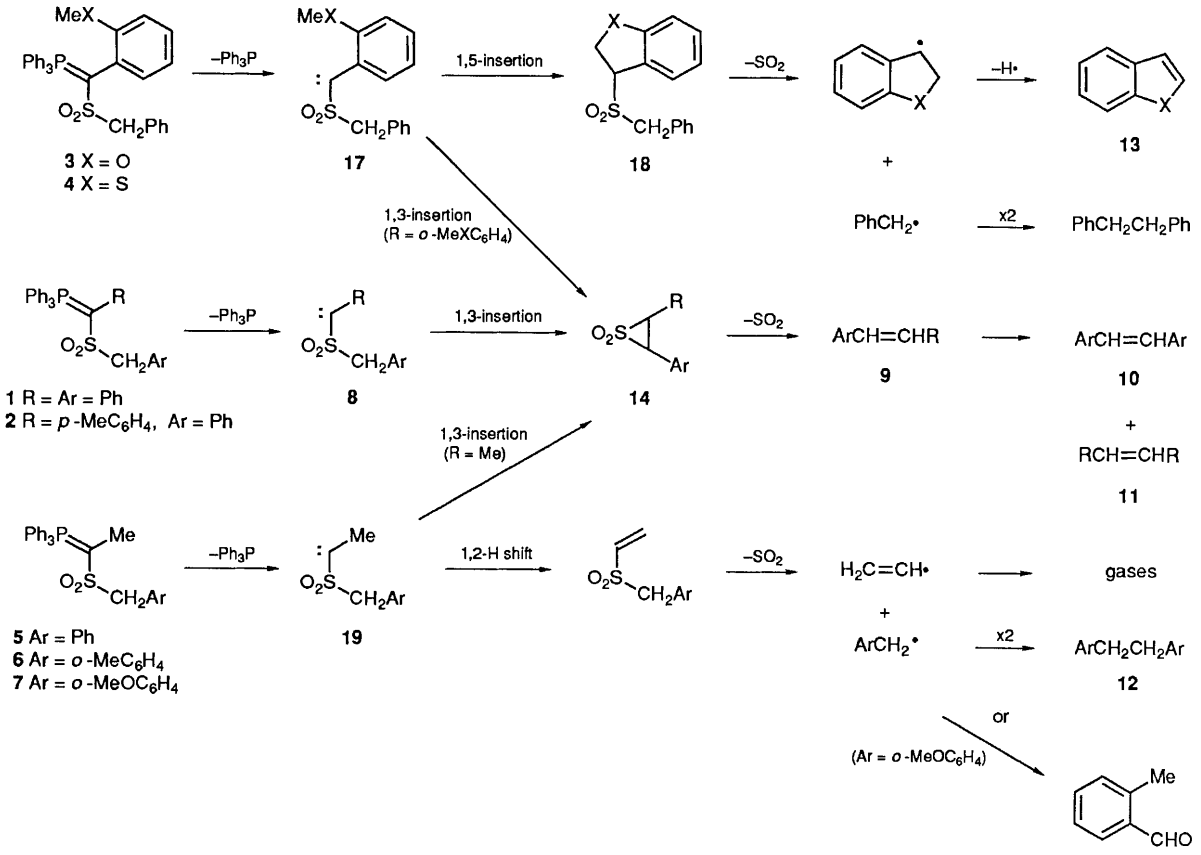
† New compounds gave satisfactory spectroscopic and analytical data.



Scheme 1

Table 1 FVP products

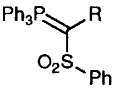
Starting ylide	Pyrolysis products (%)				
	9	**10**	**11**	**12**	**13**
1	77	—	—	—	—
2	47	6	9	—	—
3	39	—	—	11	14
4	5	—	—	29	58
5	24	7	(gas)	49	—
6	7	9	(gas)	34	—
7	6	5	(gas)	(22)	—

aromatises by loss of a H atom to **13**, while the other dimerises to give bibenzyl.

For the three remaining compounds **5**, **6** and **7**, the products **9** and **10** were formed (but-2-ene **11** was presumed to be present but was not isolated), but the major process was now the formation of benzyl radical products **12**. The presumed intermediate **19** can now undergo a 1,2-H shift to give the vinyl sulphone. Loss of SO_2 from this would give vinyl radical, which presumably goes on to gaseous products, and the benzyl radical which dimerises or, in the case of *o*-methoxybenzyl,[9] isomerises with loss of H• to *o*-tolualdehyde.

Although the extrusion of phosphines from phosphorus ylides to give carbenes is unusual, it has been proposed for alkoxy-[10] and acyloxy-alkylidenetriphenylphosphoranes.[11] Further experiments to demonstrate the intermediacy of sulphonylcarbenes **8** in the processes described here are in progress.

It is interesting to note that, in contrast to the behaviour observed here, a variety of arenesulphonyl ylides **20** undergo exclusive extrusion of Ph_3PO upon FVP to give complex and intractable products. The reason for this difference is unclear, but it may be related to subtle differences in the structure and electron distribution in the two systems. In particular X-ray structure determinations[12] of **1** and **20**, (R = Et) show the non-bonding P–O distance to be 0.1 Å shorter in the latter case (2.88 *vs.* 2.97 Å).



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References

1 S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1959, 3874; R. A. Aitken and J. I. Atherton, *J. Chem. Soc., Chem. Commun.*, 1985, 1140, and references therein.
2 H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.
3 A. M. van Leusen, B. A. Reith, A. J. W. Iedema and J. Strating, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 37.
4 B. A. Reith, J. Strating and A. M. van Leusen, *J. Org. Chem.*, 1974, **39**, 2728.
5 B. C. Smith and G. H. Smith, *J. Chem. Soc.*, 1965, 5516; E. Fluck and H. Binder, *Z. Anorg. Allgem. Chem.*, 1967, **354**, 139.
6 R. J. Mulder, A. M. van Leusen and J. Strating, *Tetrahedron Lett.*, 1967, 3057.
7 B. E. Sarver, M. Jones and A. M. van Leusen, *J. Am. Chem. Soc.*, 1975, **97**, 4771, and references therein.
8 M. Hrytsuk, N. Etkin and T. Durst, *Tetrahedron Lett.*, 1986, **27**, 5679.
9 J. I. G. Cadogan, J. B. Husband and H. McNab, *J. Chem. Soc., Perkin Trans. 2*, 1983, 697.
10 G. Wittig and W. Böll, *Chem. Ber.*, 1962, **95**, 2526.
11 E. Anders, T. Clark and T. Gassner, *Chem. Ber.*, 1986, **119**, 1350.
12 R. A. Aitken, M. J. Drysdale, G. Ferguson and A. J. Lough, manuscript in preparation.