

Flash Vacuum Pyrolysis of Alkoxy carbonyl/Sulfinyl Stabilised Phosphorus Ylides: Generation and Intramolecular Insertion of Alkoxy carbonyl(sulfenyl)carbenes

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Flash vacuum pyrolysis of phosphorus ylides stabilised both by ester and sulfinyl groups results mainly in extrusion of Ph_3PO to generate alkoxy carbonyl(sulfenyl)carbenes; these undergo intramolecular insertion into CH of the alkoxy carbonyl group giving β -lactones which under the conditions lose CO_2 to afford alkenyl sulfides.

Although the thermal extrusion of Ph_3PO from α -acylphosphonium ylides **1** to give alkynes is well established,¹ the corresponding reaction of ylides bearing other oxygen-containing functional groups on the α -position has been little investigated. Isolated reports of Ph_3PO extrusion from α -nitroso² and α -nitro ylides³ have appeared but, as we recently described, both sulfonyl ylides **2**⁴ and sulfinyl ylides **3**⁵ undergo loss of Ph_3P rather than Ph_3PO upon flash vacuum pyrolysis (FVP) to give products derived from the corresponding carbenes. We now report the preparation and pyrolytic behaviour of ylides **4**, stabilised both by α -alkoxy carbonyl and α -sulfinyl groups, which do lose mainly Ph_3PO .

The preparation of ylides **4** has only been described in two previous papers: for $\text{R}^2 = \text{CH}_2\text{Ph}$ by addition of an ester stabilised ylide to phenylsulfine,⁶ and for a wide variety of R^2 by reaction of the alkoxy carbonyl ylide with a sulfinyl chloride as shown.⁷ Using the latter method, together with the improved preparation of sulfinyl chlorides,⁸ ylides **4a–k** were obtained in moderate to good yield (Table 1) as stable, colourless solids with a distinctive doublet ($^1J_{\text{P-C}}$ 118–123 Hz) due to the ylide carbon in their ^{13}C NMR spectra (see Table 1), although these were frequently complicated by restricted rotation of the alkoxy carbonyl group with coalescence near to room temperature.

When the compounds were subjected to FVP at 500–600°C and 10^{-2} Torr (1 Torr \approx 133.3 Pa) (contact time *ca.* 10^{-2} s) there was predominant extrusion of Ph_3PO to give alkenyl sulfides **5** together with varying amounts of Ph_3P and sulfides **6** (Table 1), all identified by comparison with authentic samples. We rationalise the formation of **5** as shown in Scheme 1 by extrusion of Ph_3PO to give carbene **7** which undergoes intramolecular CH insertion to generate β -lactone **8**. Under

the pyrolysis conditions this extrudes CO_2 in a well-known process⁹ to give **5** (as a mixture of *E* and *Z* isomers for $\text{R}^1 \neq \text{H}$). This mechanism is consistent with the result of a ^{13}C labelling study in which samples of **4i** enriched to 5% ^{13}C at the carbonyl and ylide carbons were prepared and pyrolysed. In the first instance FVP gave unlabelled products while, in the second, enhancement of the signals at δ_{C} 121.1 and 122.9 corresponding to the C-1 carbon of the propenyl group in the *E* and *Z* isomers of **5i** was observed. As far as we are aware this is the first unambiguous report of the generation of alkoxy carbonyl(sulfenyl)carbenes.[†] The behaviour observed here is in excellent agreement with that of bis(methoxycarbonyl)carbene generated by FVP of the diazomalonate,¹¹ which underwent insertion to give a β -lactone followed by loss of CO_2 to afford methyl acrylate. Photochemical generation of an ethoxycarbonylcarbene has allowed isolation of the β -lactone resulting from insertion in one instance,¹² and the formation of β -lactams by insertion of (dialkylamino)carbonylcarbenes is quite well known.¹³ Close analogies can also be found in recent studies of carbenes derived from α -diazophosphonates¹⁴ and α -diazophosphonamides¹⁵ where insertion to form four-membered rings is observed, and in the former case is accompanied by extrusion of metaphosphate to give alkenes.

The formation of sulfides **6** may occur by a variety of different routes involving either loss of Ph_3PO followed by two molecules of CO or loss of Ph_3P followed by CO and CO_2 . Some insight into the processes occurring has been obtained by separate pyrolysis of proposed intermediates **9–11**. Thus, FVP of **9f** at 600°C gave partial conversion to **10f**, accompanied when the temperature was raised to 750°C by **6f**. In the case of **9g**, FVP at 600°C produced both **10g** and **6g**. Similarly, FVP of **11a** and **11i** gave the corresponding sulfides **6** at 750°C and 600°C, respectively. It seems therefore that the conversions of **9** to **10** and both **10** and **11** to **6** are feasible under the conditions involved, but **9** to **11** is not.

The predominant extrusion of Ph_3PO observed here contrasts with the behaviour of the closely related ylides **3**

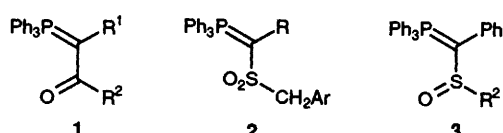
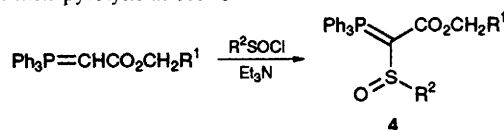


Table 1 Formation of ylides **4** and results of their pyrolysis at 600°C



	R^1	R^2	Yield of 4 (%)	δ_{p}	δ_{C} (ylide)	Products from FVP of 4 (%)			
						Ph_3PO	Ph_3P	5	6
a	H	Ph	64	28.2	35.7	93	7	14	22
b	H	<i>p</i> -Me-C ₆ H ₄ -	30	28.3	36.2	90	10	11	25
c	H	<i>p</i> -Br-C ₆ H ₄ -	53	28.2		100	0	5	11
d	H	Me	13	27.6		30	70	20	—
e	H	Et	35	27.4		22	78	10	—
f	Me	Ph	71	28.1	36.0	100	0	10	7
g	Me	<i>p</i> -Me-C ₆ H ₄ -	41	28.35	36.4	70	30	51	1
h	Me	<i>p</i> -Br-C ₆ H ₄ -	60	28.3		100	0	53	11
i	Me	<i>p</i> -Cl-C ₆ H ₄ -	72	28.3	36.0	40	60	17	1
j	Me	Et	44	27.5	37.0	34	66	36	<1
k	Et	<i>p</i> -Me-C ₆ H ₄ -	3	28.2		40	60	34	—

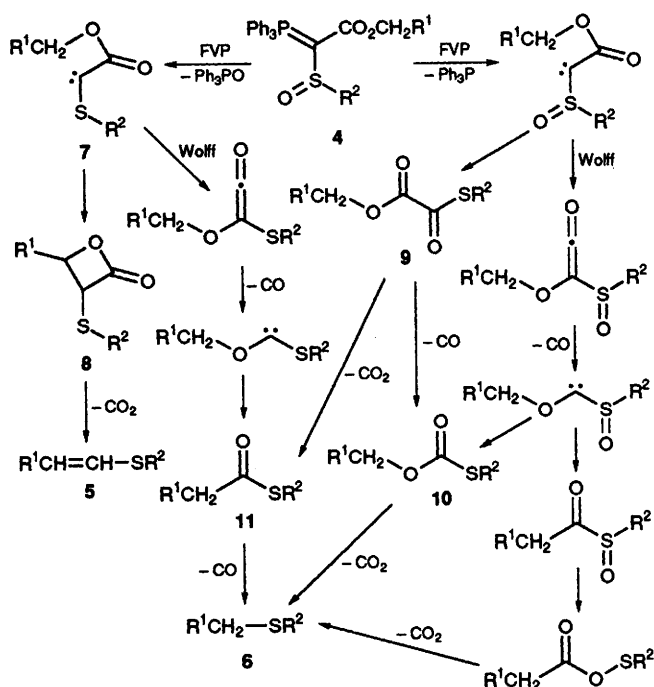
where Ph_3P is generally eliminated.⁵ This appears to be due to the greater polarisation of the ylide bond in the case of **4**, a feature consistent with the NMR data for the two compound types. Thus, ylides **3** (δ_{P} 18.7–20.4, δ_{C} (ylide) 47.1–52.2) exist more in the uncharged form **12** where extrusion of Ph_3PO is difficult, while for **4** the introduction of the ester group has caused a greater polarisation of the bond towards the extreme form **13**, reflected in deshielding of the phosphorus and shielding of the carbon (see Table 1) and facilitating extrusion of Ph_3PO .

Finally, it is worth noting that the sulfinyl chlorides used to prepare **4** are readily derived from the corresponding thiols⁸ and so in favourable cases this provides a feasible if unusual three-step route for conversion of thiols R^2SH to alkenyl

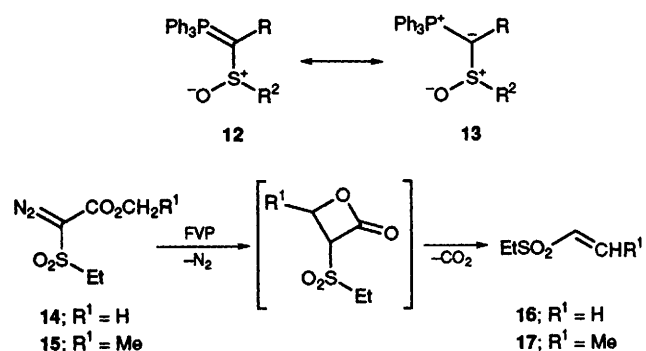
sulfides **5**, which are of some interest as synthetic intermediates.¹⁶ An analogous process is also observed for alkoxy-carbonyl(sulphonyl)carbenes and FVP of **14** and **15** at 600°C gives alkenylsulfones **16** and **17** in yields of 30 and 10% respectively (Scheme 2).

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Scheme 1



Footnote

† A study in which the apparent addition products of $\text{MeO}_2\text{C}(\text{MeS})\text{C}$: to alkenes were obtained by base-induced α -elimination from the α -chloroester seems unlikely to involve the free carbene since the reactions were performed in the presence of SnCl_4 (ref. 10).

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