Flash Vacuum Pyrolysis of Sulfinyl Stabilised Phosphorus Ylides: Generation and Reactivity of Sulfinylcarbenes

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Flash vacuum pyrolysis of α-alkanesulfinyl phosphorus ylides results mainly in extrusion of Ph_3P to give thioesters, presumably by 1,2-oxygen transfer in the initially formed sulfinyl carbenes; for α-arenesulfinyl ylides loss of Ph_3PO to give additional products is also observed.

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. Sulfonyl cyanides have been prepared by spontaneous extrusion from α-nitroso ylides **2** at −40 °C,[2] and there is evidence for extrusion of Ph_3PO from α-nitro ylides **3** to give nitrile oxides,[3] but we recently reported that sulfonyl ylides **4** undergo loss of Ph_3P rather than Ph_3PO upon flash vacuum pyrolysis (FVP) to give products derived from sulfonylcarbenes.[4] We now report the preparation and pyrolytic behaviour of representative α-sulfinyl ylides **5**.

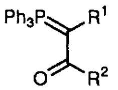
The sulfinyl ylides are little known and there were only two reports,[5] both involving additional stabilisation by an ester group, until the (sulfinylmethylene)diphenylmethylphosphoranes were recently described,[6] formed by reaction of a lithium phosphonium diylide with sulfinate esters. The required ylides **5** were readily formed in low to moderate yield (Table 1) in analogy to the acyl ylides **1**, by reaction of $Ph_3P{=}CHPh$ (2 equiv.) with sulfinyl chlorides RS(O)Cl. The sulfinyl chlorides, which are notoriously unstable and difficult to purify, were used directly as obtained from the improved method recently reported[7] involving treatment of RSH with 2 equiv. SO_2Cl_2 and 1 equiv. AcOH. The ylides were recognised easily from the characteristic doublet ($^1J_{P-C}$ 122–128 Hz) due to the ylide carbon in their ^{13}C NMR spectra (see Table 1).

For the alkanesulfinyl ylides **5a–c**, FVP at 500 °C and 10^{-2} Torr (contact time *ca.* 10^{-2} s) resulted mainly in extrusion of Ph_3P to give the thioesters **6** (Table 1). This can be explained by a 1,2-O-transfer in the initially formed sulfinylcarbenes *via* the zwitterionic oxathirane intermediate shown. Sulfinylcarbenes are a little known class of reactive intermediates,[8] but this type of oxygen transfer has been observed before in two cases.[9] The analogous rearrangement of nitrocarbenes to acynitroso compounds has been described,[10] as has 1,4-O-transfer from sulfur in an *N*-sulfonylimidoylcarbene to give the sulfinylimidoyl ketone.[11]

For **5a–c** there was also some loss of Ph_3PO to give unknown

Table 1 Formation of ylides **5** and results of their pyrolysis at 500 °C

R	Yield of **5** (%)	δ_P	δ_C (ylide)	Products from FVP of **5** (%)							
				Ph_3P	Ph_3PO	**6**	**8**	**9**	**10**	**11**	**12**
a Et	24	+19.7	47.9	80	13	53	—	—	—	—	—
b Pr^i	33	+20.2	47.2	84	9	37	—	—	—	—	—
c CH_2Ph	4	+18.7	47.1	50	40	30	—	2	10	—	—
d Ph	29	+20.4	52.2	64	32	20	—	4	10	10	8
e p-Me-C_6H_4	45	+20.2	52.1	82	15	25	5	—	—	6	20
f p-Cl-C_6H_4	31	+19.7		27	67	9	18	7	7	17	25



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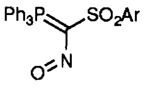

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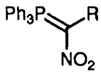

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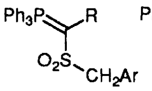

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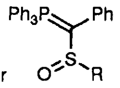

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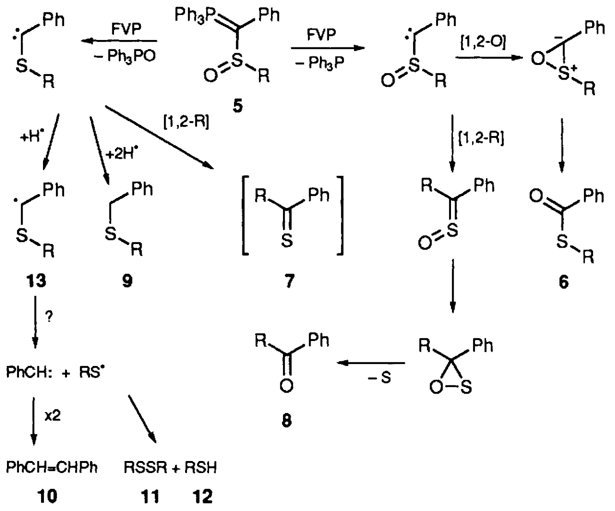

Scheme 1

products, and for the arenesulfinyl ylides **5d–f** competing processes were more important, although **6** was still formed in each case.† The most obvious feature in these cases was the production of an intense dark-blue colour in the cold trap that faded rapidly upon warming. This is attributed to the thioketone **7** although it was only present in trace quantities and could not be detected spectroscopically. The formation of this product may be due to rearrangement of the thiocarbene resulting from Ph_3PO extrusion. A major product for **5e,f** was the ketone **8** (Scheme 1) which most likely results from rearrangement of the sulfinylcarbene to a sulfine followed by loss of sulfur. A closely related example, dimethylvinyl(p-toluenesulfinyl)carbene, has been reported to give the ketone in excellent yield in an analogous way,[12] and the absence of this process for **5a–c** reflects the poorer migratory aptitude of alkyl *vs.* aryl groups. The remaining products can be accounted for by alternative reactions of the thiocarbene resulting from extrusion of Ph_3PO. The benzyl sulfide **9** (Scheme 1) is clearly formed by hydrogen atom abstraction, but the formation of stilbene **10** is more difficult to explain. Although the disulfide **11** and thiol **12** may be formed by a variety of radical processes which generate $RS^•$, it is attractive to speculate that all three products may result as shown from an α-elimination process of radical **13** formed by abstraction of single hydrogen atom by the thiocarbene, although we are not aware of any precendent for this process. A further complication is the possibility of disproportionation of **5** in the inlet tube which has been observed for other sulfinyl ylides,[13] and would lead to further products from pyrolysis of sulfenyl and sulfonyl ylides.

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† In Table 1 the balance of the phosphorus products is accounted for in each case by Ph_3PS, presumably formed by interaction of Ph_3P with sulfur contining products.