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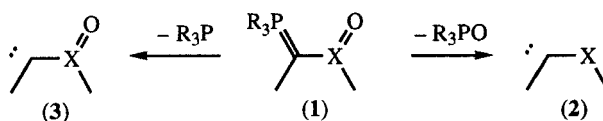
PYROLYSIS OF STABILISED PHOSPHORUS YLIDES AS A ROUTE TO NEW HETERO CARBENES

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Abstract: Flash vacuum pyrolysis of sulphonyl- and sulphinyl-stabilised phosphorus ylides results in loss of either phosphine or phosphine oxide to generate thio-, sulphinyl- and sulphonyl-carbenes which undergo a variety of rearrangement and insertion processes to give stable products. The first case of phosphine extrusion from a β -oxo ylide is reported, giving access to benzotriazolyl acetyl carbene which rearranges to an acetyl benzotriazine and 2-cyanoacetophenone.

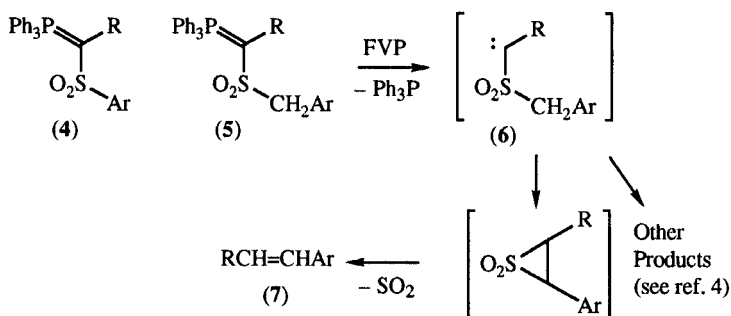
Thermal extrusion of Ph_3PO from both phosphorus ylides¹ and phosphinimines² stabilised by an α -acyl group is well known to lead to alkynes and nitriles, respectively, and in the former case the use of flash vacuum pyrolysis (FVP) gives improved yields in many cases.³ We have carried out a detailed study of the pyrolytic behaviour of a variety of phosphorus ylides stabilised by other oxygen-containing functional groups, notably sulfoxide and sulphone. As described below, this has revealed processes involving loss of both phosphine and phosphine oxide, so that in general (1) may give either (2) or (3) depending both on the nature of X and the substituents present.



SULPHONYL YLIDES

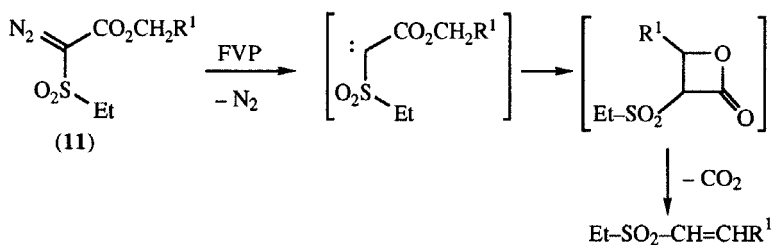
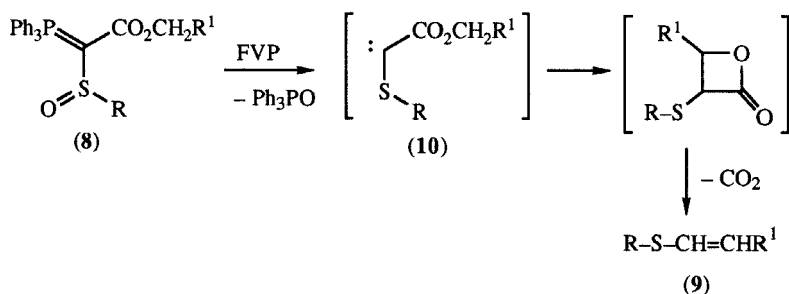
The results for sulphonyl stabilised ylides have already been described briefly.⁴ Compounds of type (4) lost Ph_3PO to give a complex mixture of products which could not be fully identified and the process was of no preparative value. In contrast the phenylmethanesulphonyl ylides (5) underwent exclusive loss of Ph_3P to give products which could be accounted for by intramolecular insertion and rearrangement of the

sulphonylcarbenes (6). In all cases the alkene products (7) were formed as shown, accompanied in some cases by other products depending on the nature of R.⁴



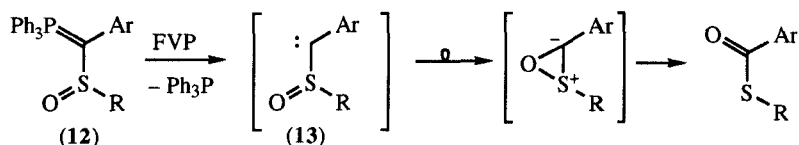
SULPHINYL YLIDES

A range of sulphonyl ylides have also been prepared by acylation of the appropriate starting ylides with sulphonyl chlorides. For the compounds of type (8) stabilised both by a sulphonyl and an ester group, Ph_3PO is lost and the final product is a vinyl sulphide (9)⁵. We believe that these reactions proceed by intramolecular insertion of the carbene (10) to give a β -lactone which loses CO_2 to afford the observed product. Support for this idea is provided by the pyrolysis of α -sulphonyl- α -diazoesters (11) which gives the expected vinyl sulphones presumably by a similar mechanism. Since (8) is prepared in two steps from RSH and the pyrolysis proceeds in good yield, this represents a viable if

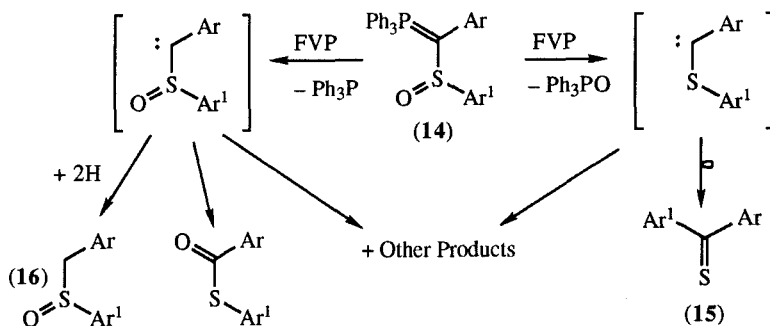


unusual route to convert thiols into vinyl sulphides.

The simpler ylides (**12**) stabilised only by the alkanesulphinyl group undergo a different process. Loss of Ph_3P is followed by rapid rearrangement of the sulphinylcarbene (**13**) by 1,2-oxygen transfer to give the thioesters.

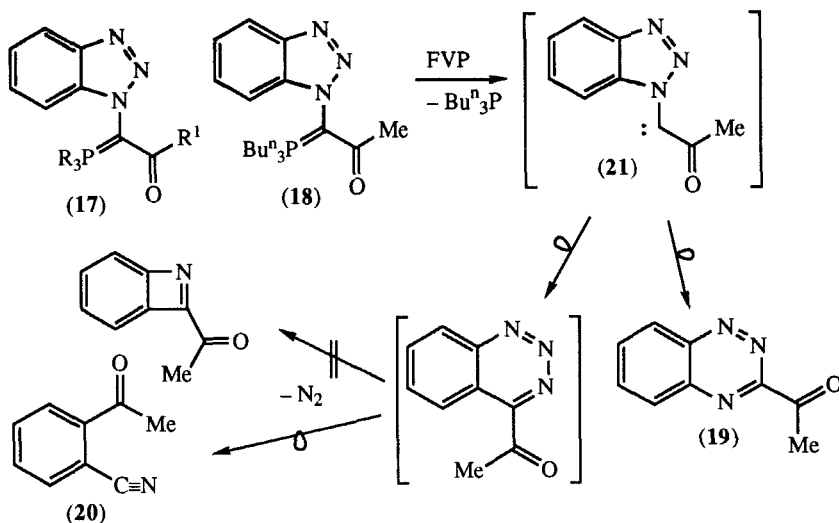


The pyrolytic behaviour of the arenesulphinyl ylides (**14**) is more complex and is not yet fully understood. Both Ph_3P and Ph_3PO are eliminated and both the resulting carbenes lead to products. The bright blue colour produced is almost certainly due to the thioketones (**15**) but these are only there in trace amounts and the colour quickly fades due to reaction with some of the other products present. These include the sulphoxide (**16**) resulting from hydrogen abstraction by one carbene, the thioester from its rearrangement, and products of radical decomposition such as diaryl sulphides.



EXTRUSION OF PHOSPHINE FROM A β -OXO YLIDE

A wide range of benzotriazolyl ylides (**17**) have been prepared and pyrolysed. They generally lose Bu^n_3PO and N_2 to give complex products. In contrast, compound (**18**) loses Bu^n_3P to give two heterocyclic products. After detailed studies these have been confirmed to be 3-acetyl-1,2,4-benzotriazine (**19**) and 2-cyanoacetophenone (**20**).⁶ As shown these products can be explained by a series of rearrangements and loss of N_2 from the new carbene (**21**). The reason for (**18**) losing Bu^n_3P and not Bu^n_3PO , an apparently unprecedented process, is not yet clear.



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