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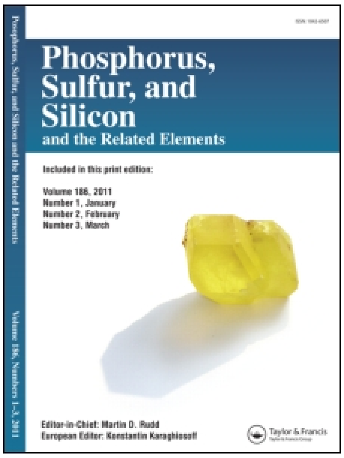

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Studies of the Reactions of 2-Substituted Dimethyl Benzoylphosphonates with Trimethyl Phosphite

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STUDIES OF THE REACTIONS OF 2-SUBSTITUTED DIMETHYL BENZOYLPHOSPHONATES WITH TRIMETHYL PHOSPHITE

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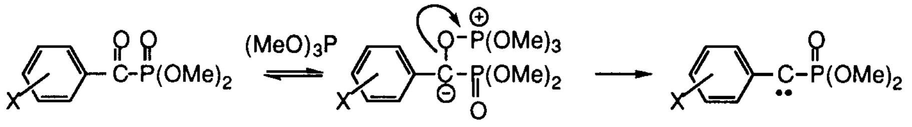
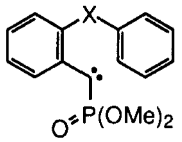
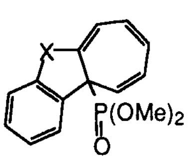
Dimethyl benzoylphosphonates (**1**) react with trimethyl phosphite to give anionic intermediates (**2**) which decompose to give carbenes (**3**) and trimethyl phosphate [1]. When suitable *ortho*-substituents are present on the benzoylphosphonate, intramolecular carbene insertion reactions can occur to give cyclic systems. With alkyl substitutents, where the length of the chain provides a choice of cyclisation pathways, insertion into an appropriate C—H bond to give a 5-membered ring has been found to be the preferred option. We have therefore been investigating the behaviour of systems, such as (**4**), where insertion into a C—H bond to give a 5-membered ring is prevented.



(1) (2) (3) + $(MeO)_3PO$



(4)



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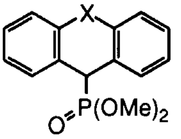

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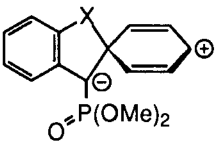

(7)

These studies have led to the formation of some novel products. For the case of (**4**; X=S) subsequent reaction leads to the formation of products including the thioxanthenyl-phosphonate (**5**; X=S) and the ring expanded product (**6**; X=S). Although the formation of (**5**; X=S) appears to involve carbene insertion into the 2'C—H bond of the phenylthio substituent in (**4**; X=S), further work with methyl-substituted derivatives has shown that the formation of (**5**; X=S) occurs via the spiro-diene system (**7**; X=S).

[1] D. V. Griffiths, P. A. Griffiths, B. J. Whitehead, and J. C. Tebby, *J. Chem. Soc. Perkin Trans. 1*, 479, (1992).