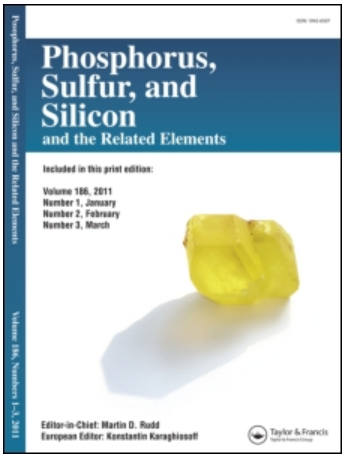

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Reactions of Dimethyl Heteroaroylphosphonates with Trialkyl Phosphite in the Presence of Proton Donors

D. Vaughan Griffiths[a]; Jayne E. Harris[a]
[a] Department of Chemistry, Queen Mary and Westfield College, University of London, London, U. K.

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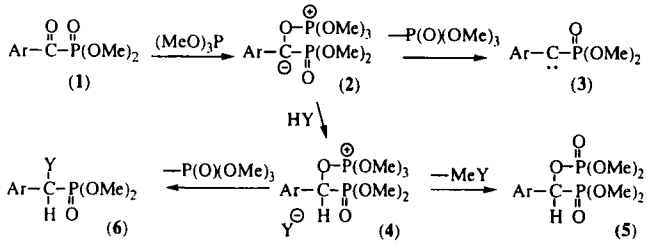
Reactions of Dimethyl Heteroaroylphosphonates with Trialkyl Phosphite in the Presence of Proton Donors

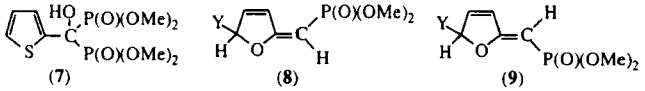
D. VAUGHAN GRIFFITHS and JAYNE E. HARRIS

Department of Chemistry, Queen Mary and Westfield College, University of London, London E1 4NS, U.K.

We have previously shown that substituted benzoylphosphonates (**1**; Ar = X-Ph) react with trimethyl phosphite to give anionic intermediates which in the absence of electrophiles decompose to give carbene intermediates (**3**). The nature of the subsequent reaction products depends on the type and position of the substituents on the aromatic ring.[1] When proton donors are present the initially formed anionic intermediates (**2**) give the quasi-phosphonium salts (**4**) which usually decompose to give the phosphonate-phosphates (**5**), although for the case of (**1**; Ar = 4-MeOPh) formation of the phosphonates (**6**) was observed.



We have now extended our studies to heteroaroylphosphonates such as (**1**; Ar = furanyl and thienyl) and observe some interesting differences. For example, while the thenoyl system (**1**; Ar = 2-thienyl) gave phosphonates of type (**6**) with methanol and phenol, the bisphosphonate (**7**) was formed in the presence of 4-toluenesulfonic acid. In contrast, formation of phosphonates (**6**) was not observed for the furoyl system (**1**; Ar = 2-furanyl) with methanol or phenol. Instead we observed involvement of the furan ring system and the formation of the isomers (**8**) and (**9**), illustrating the consequences of the reduced aromaticity and increased diene character of the furan ring system.



References

[1] D.V. Griffiths, J.E. Harris and B.J. Whitehead, *J. Chem. Soc. Perkin Trans.* **1**, 2545, (1997) and references therein.