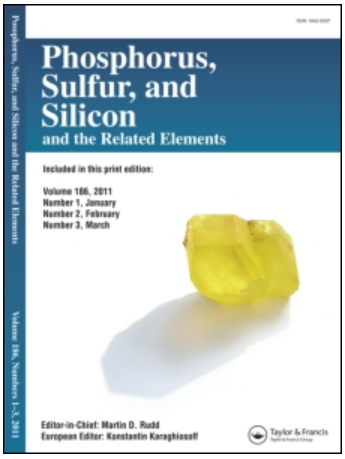

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A New Route to Some Novel Phosphole Derivatives

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A New Route to Some Novel Phosphole Derivatives

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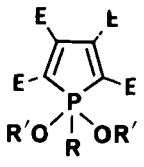
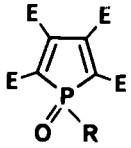
Previous work has shown that the unstable five co-ordinate phospholes (1; R=alkoxy, R'=alkyl) produced in the reaction of trialkyl phosphites with a two molar equivalent of dimethyl acetylenedicarboxylate can be converted into the novel phospholes (2; R=alkoxy) by treatment with hydrogen bromide at low temperature. We have now shown that a similar approach can be used to generate the phospholes (2; R=alkyl, aryl) by using dialkyl alkylphosphonites or dialkyl arylphosphonites rather than trialkyl phosphites. However, the reduced stability of the phosphorane intermediates (1; R=alkyl, aryl, R'=alkyl) relative to those produced in the trialkyl phosphite reactions means that these trapping reactions are difficult to carry out successfully.

Fortunately, the stable cyclic ylides (3) produced by the rearrangement of the phosphoranes (1) have also proved to be suitable precursors for the production of the phospholes (2; R=alkoxy, alkyl, aryl). Thus protonation and dealkylation of the cyclic ylides (3; R=alkoxy, alkyl, aryl, R'=alkyl) led to the formation of the corresponding phospholenes (4) which then eliminated a molecule of alcohol to give the phospholes (2; R=alkoxy, alkyl, aryl).



(1)



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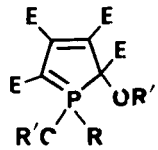

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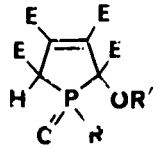

(4)

(E = CO_2Me)