

## Trapping of Reactive Intermediates from Phosphites and Dimethyl Acetylenedicarboxylate. Diversion of Reaction Pathway towards Stable Phosphole Derivatives

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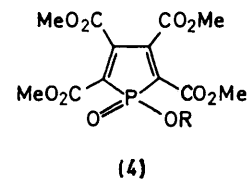
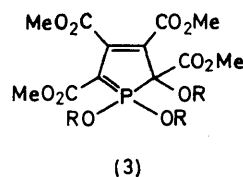
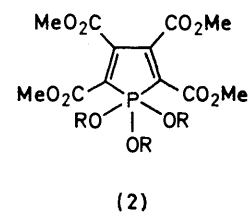
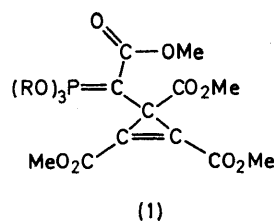
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**Summary** Trialkyl phosphites and dimethyl acetylenedicarboxylate react at  $-50\text{ }^{\circ}\text{C}$  to give the cyclopropenyl-methylene trialkoxyphosphonium ylide (**1**), which at  $-10\text{ }^{\circ}\text{C}$  cyclises to the novel five-co-ordinate phosphorane (**2**); at  $20\text{ }^{\circ}\text{C}$  the phosphorane (**2**) rearranges to the cyclic ylide (**3**), whilst hydrogen bromide gas at  $-10\text{ }^{\circ}\text{C}$  converts the phosphorane (**2**) into a stable phosphole derivative (**4**).

THE reactions of triphenylphosphine with electrophilic acetylenes are good examples of relatively simple reactants producing quite complex products.<sup>1</sup> The mechanisms by necessity must involve a number of reactive intermediates but there has been little direct evidence on their characterisation.<sup>2</sup> By the use of trialkyl phosphites in place of triphenylphosphine, the reaction with dimethyl acetylenedicarboxylate (2 equiv.) in toluene at  $-50\text{ }^{\circ}\text{C}$  gives, after 1–2 h, an almost quantitative yield of the ylides (**1**), observed in their low-temperature  $^{31}\text{P}$  n.m.r. spectra as two rotamers whose relative proportions were shown to be temperature-dependent. The rotamers arise from restricted rotation about the bond to the  $\alpha$ -methoxycarbonyl group. The ylide (**1**, R = Me) had  $\delta(^{31}\text{P})$  61.6 and 59.4 p.p.m.† and  $\delta(^{13}\text{C})$  41.45 ( $^1J_{\text{PC}}$  225 Hz) and 36.04 ( $^2J_{\text{PC}}$  18 Hz) p.p.m. At  $-10\text{ }^{\circ}\text{C}$  the ylides convert quantitatively, during 15–30 min, into the five-co-ordinate phosphoranes (**2**) which are stable for many hours at this temperature. These compounds possess characteristically high-field signals in their  $^{31}\text{P}$  n.m.r. spectra [(**2**, R = Me);  $\delta(^{31}\text{P})$   $-37.4$  p.p.m.] and the proton-coupled spectrum confirmed that three alkoxy-groups were still bound directly to the phosphorus atom.

The symmetrical structure was confirmed by the presence of only seven different chemical shifts in the  $^{13}\text{C}$  n.m.r. spectrum, each with the appropriate shift and coupling parameters. These structures are quite novel, although some of the first suggestions for the formation of organic five-co-ordinate phosphoranes concerned the reactions of triphenylphosphine with electrophilic acetylenes.<sup>3</sup>



At  $20\text{ }^{\circ}\text{C}$  they have half-lives of 10–12 min, being smoothly converted into the stable cyclic ylides (**3**). The ethyl analogue [(**3**, R = Et);  $\delta(^{31}\text{P})$  80.5 p.p.m.] was isolated in 55% yield as a colourless solid.‡ Low-temperature  $^{31}\text{P}$

† Positive shifts are downfield with respect to 85% phosphoric acid.

‡ The isolated products gave correct elemental analyses.

n.m.r. spectroscopy showed the presence of four rotamers as predicted for this structure.  $^1\text{H}$ ,  $^{13}\text{C}$ , and the proton-coupled  $^{31}\text{P}$  n.m.r. spectra showed that one of the alkoxy-groups had migrated from phosphorus to the adjacent carbon atom.

The reaction can be diverted from the rearrangement pathway by passing hydrogen bromide gas (1 equiv.) into the solution of the phosphorane (**2**) at  $-10^\circ\text{C}$ . The

phosphole derivatives [(**4**, R = Et);  $\delta(^{31}\text{P})$  34.99 p.p.m., t] and [(**4**, R = H);  $\delta(^{31}\text{P})$  35.41 p.p.m., s] were isolated in 25–30% yields.† Dimerisation, which occurs rapidly for the parent phosphole oxide, was not observed for these products.<sup>4</sup>

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<sup>1</sup> N. E. Waite and J. C. Tebby, *J. Chem. Soc. C*, 1970, 386; M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *ibid.*, 1968, 1609.

<sup>2</sup> N. E. Waite, D. W. Allen, and J. C. Tebby, *Phosphorus*, 1971, 1, 139.

<sup>3</sup> A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 1961, 2126; G. S. Reddy and C. D. Weis, *J. Org. Chem.*, 1963, 28, 1822.

<sup>4</sup> D. A. Usher and F. H. Westheimer, *J. Am. Chem. Soc.*, 1964, 86, 4732.