Carbene Intermediates in the Reaction of Trialkyl Phosphites with Dialkyl Aroylphosphonates: Formation of Novel Quasiphosphonium Ylides

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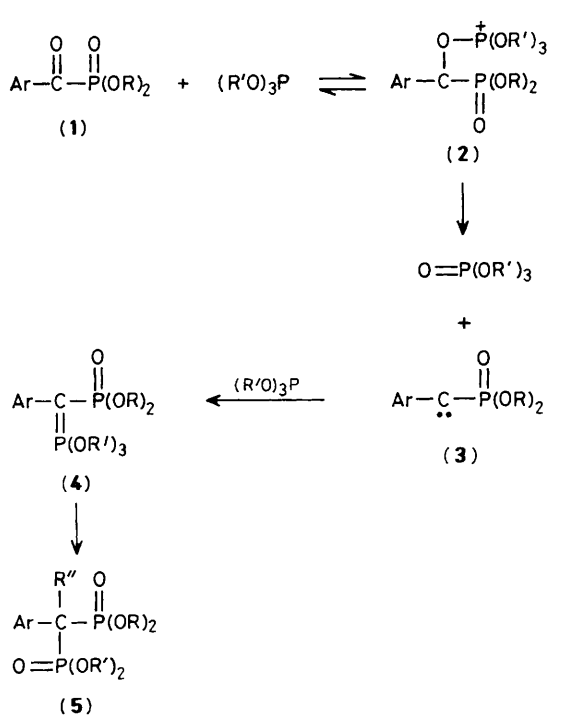
Reaction of trialkyl phosphites with dialkyl aroylphosphonates leads to the formation of anionic intermediates which, in the absence of electrophiles, undergo cleavage at temperatures above about 80 °C to give carbene intermediates; these undergo intramolecular carbene insertion reactions or are trapped by trialkyl phosphites to give novel ylides.

The reaction of trialkyl phosphites with dialkyl aroylphosphonates (**1**) in the presence of electrophiles has been shown to involve an initial attack of the phosphorus atom at the carbonyl oxygen to give carbanionic reactive intermediates (**2**)[1,2] which then readily react with the electrophile. We now have compelling evidence to show that under some circumstances these carbanionic intermediates can also eliminate a molecule of trialkyl phosphate to form carbenes.

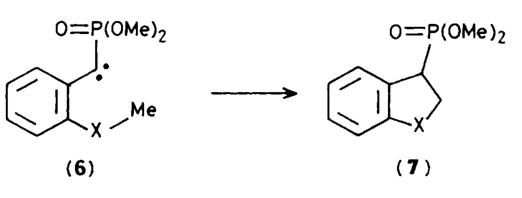
At room temperature the reaction between trialkyl phosphites and dialkyl aroylphosphonates proceeds at a significant rate only if a suitable electrophile is present to trap the anionic intermediate as it forms. However, in the absence of an electrophile the reaction can be made to proceed at temperatures above about 80 °C. Under these conditions benzoylphosphonates such as (**1**; Ar = Ph, 4-MeO-C_6H_4, 4-Me-C_6H_4, 4-Cl-C_6H_4) react initially to form novel ylides (**4**). For example, the reaction of the aroylphosphonate (**1**; Ar = 4-MeO-C_6H_4, R = Me) with triethyl phosphite at 85 °C for 12 h led to the formation of the ylidic phosphonate (**4**; Ar = 4-MeO-C_6H_4, R = Me, R′ = Et) [δ_P 49.4, 31.6 p.p.m.,† J_{PP} 94 Hz; δ_C (α-C) 28.23, J_{PC} 211, 223 Hz] in virtually quantitative yield. In some case, particularly where R′ = Me, the quasiphosphonium ylides undergo thermal rearrangement during the course of the reaction to give diphosphonates. Thus, the initially formed ylide (**4**; Ar = 4-MeO-C_6H_4, R = R′ = Me) underwent rearrangement to give the diphosphonate (**5**; Ar = 4-MeO-C_6H_4, R = R′ = R″ = Me) under the conditions required to generate the ylide. If the ylides (**4**) are treated with dilute aqueous acid they are readily converted into the corresponding diphosphonates (**5**; R″ = H). We consider that the formation of the ylides is best explained by postulating that, on heating, the carbanionic intermediates (**2**) are undergoing cleavage of the α-C–O bond to give carbenes (**3**) which then react rapidly with the trialkyl phosphite present to give the observed ylides (**4**). The formation of ylides by the reaction of carbenes with other three co-ordinate phosphorus compounds is well established.[3]



We have conclusively demonstrated the involvement of a carbene intermediate in the reaction of the phosphonate (**1**; Ar = 2-Et-C_6H_4, R = Me) with trimethyl phosphite at 106 °C. Dimethyl indan-1-ylphosphonate (**7**; X = CH_2) [δ_P 31.3 p.p.m.,† δ_C (CH) 41.97 (d, *J* 143 Hz), (CH_2) 31.69 (d, *J* 4 Hz), and 26.64 (d, *J* 4 Hz), M^+ 226] (~40%) was formed together with a similar quantity of the ylide (**4**; Ar = 2-Et-C_6H_4, R = R′ = Me) (δ_P 50.48, 29.26 p.p.m.,† J_{PP} 98 Hz). The cyclisation involving the ethyl group in the phosphonate (**1**; Ar = 2-Et-C_6H_4, R = Me) to give the indan ring system in (**7**; X = CH_2) cannot be adequately explained other than by the formation of the carbene intermediate (**6**; X = CH_2) which then undergoes an intramolecular carbene insertion reaction.

We believe that the cyclisation of some other *ortho*-substituted aroylphosphonates upon heating with trialkyl phosphite,[4] previously explained in terms of an ionic mechanism, can also be better explained in terms of an intramolecular carbene insertion mechanism. Interestingly, we found that the reaction of (**1**; Ar = 2-MeO-C_6H_4, R = Me) with trimethyl phosphite at 85 °C led to the formation of not only the previously reported bicyclic system (**7**; X = O) but also the ylidic phosphonate (**4**; Ar = 2-MeO-C_6H_4, R = R′ = Me).

Although carbene intermediates have been suspected in a number of reactions involving the deoxygenation of carbonyl groups by trivalent phosphorus compounds it has proved to be difficult until now to obtain conclusive evidence to support such a mechanism.[5a] In contrast, the deoxygenation of nitro groups by trivalent phosphorus compounds such as trialkyl phosphites to give nitrenes is well established[5b] and has



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

substantial synthetic potential. This new method should also have synthetic potential.

Received, 21st February 1986; Com. 229

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