Tetrahedron Letters No. 24, pp 2203 - 2204.
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0040-4039/79/0608-2203$02.00/0

THE OBSERVATION OF AN OXAPHOSPHETANE INTERMEDIATE IN THE PHOSPHONATE MODIFICATION OF THE WITTIG OLEFIN SYNTHESIS

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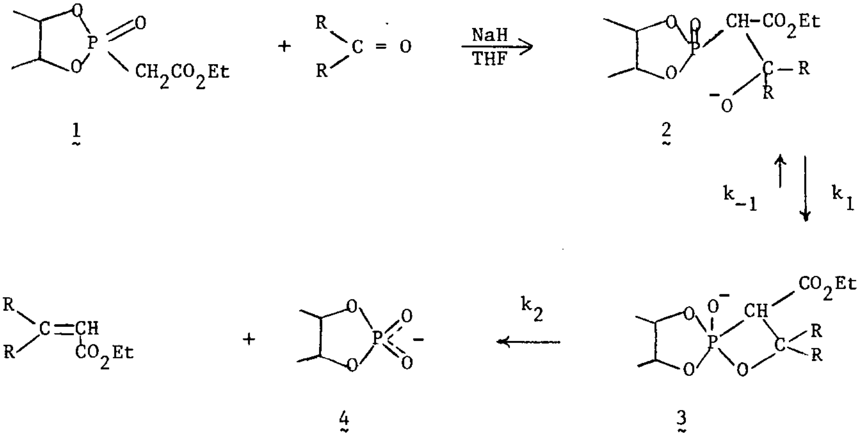
Abstract: A signal at high field is observed in the ^{31}P nmr of the reaction mixtures of some ketones with a five-membered cyclic phosphonate.

It has been demonstrated that reactions of non-stabilized phosphorus ylids with aldehydes or ketones, that lead to olefins, involve oxaphosphetanes[2-5] and betaines[6] as intermediates. In contrast in the reactions of stabilized ylids[7,8] which lead predominantly to (E) olefins,[9] only betaines have been so far observed,[5] while the question of the nature of oxaphosphetanes (whether intermediates or transition state) has not yet been settled.

Recently we reported that in contrast to acyclic phosphonates, reactions of the five-membered cyclic phosphonate 1 with aldehydes lead preferentially to (Z) olefins.[10] This was interpreted as being the consequence of a decrease in the reversibility of the reaction, due to ring-strain effect, namely that the strain in the five-membered dioxaphospholane ring is relieved upon conversion to a pentacoordinated phosphorus derivative.[11,12] Due to this strain effect betaine 2 is expected to cyclize at a faster rate to 3, which in turn would decompose slower than analogous intermediates derived from acyclic phosphonates. Consequently we postulated[10] that the reaction of the cyclic phosphonate involves an oxaphosphetane intermediate.



One necessary condition for success in observing 3 by FT ^{31}P nmr is to find conditions and substrates with which the reaction would proceed through the entire duration of the measurement. Initial experiments showed that aliphatic aldehydes and ketones do not fulfill this requirement as they react with **1** very fast and that their reactions are complete in a few seconds after mixing even at -60° C., before data from a significant number of scans of spectra can be accumulated.

The reaction of benzophenone and **1** was considerably slower. At -25° C in THF it showed in the ^{31}P nmr spectrum[17] peaks at -54 and -15 ppm, corresponding to the ylid of **1** and to phosphate **4**[18] respectively, indicating that the reaction does proceed, but that the concentration of **3** is too low to be observable.

At this point it was considered that since the steady state concentration of **3** is directly proportional to $k_1/k_{-1} + k_2$, and since k_1 is more strongly temperature dependent than k_{-1} and k_2, raising the temperature will result in increase of the concentration of **3**. Indeed when the reaction was followed by ^{31}P nmr at 0° C, the spectrum that was recorded after 1000 scans showed a peak at +34 ppm in addition to those at -54 and -15. We could also observe signals at +32 ppm when phosphonate **1** was reacted with cyclopropyl phenyl ketone or p-anisyl cyclopropyl ketone, in both cases at room temperature.

The appearance of the signals at high field[19] in the reactions of cyclic phosphonate **1** clearly indicate that a pentacoordinated phosphorus intermediate is involved in the phosphonate modification of the Wittig olefin synthesis.

References and Notes

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12. Pentacoordinated phosphorus compounds that contain one or no ring have been shown to possess trigonal bipyramid structure (TBP).[10] However, recently it was found that spirophosphoranes containing two five-membered rings[13-15] or one four- and one five-membered ring[16] deviate from an ideal TBP, and are of a rectangular pyramid structure (RP). Following this it is reasonable to assume that **3** is also an RP with the two rings pointing towards the base and the oxide ion pointing towards the apex of the pyramid.
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(Received in USA 28 February 1979)