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REACTIONS OF DIALKYL HYDROGEN PHOSPHONATES AND TRIALKYL PHOSPHITES WITH TETRAPHENYLCYCLOPENTADIENONE

A.J. Floyd* and K.C. Symes
School of Chemistry and Chemical Engineering
Bath University of Technology
Bath, Somerset.

G.I. Fray, G.E. Gymer, and A.W. Oppenheimer
School of Chemistry
University of Bristol
Bristol BS8 1TS.

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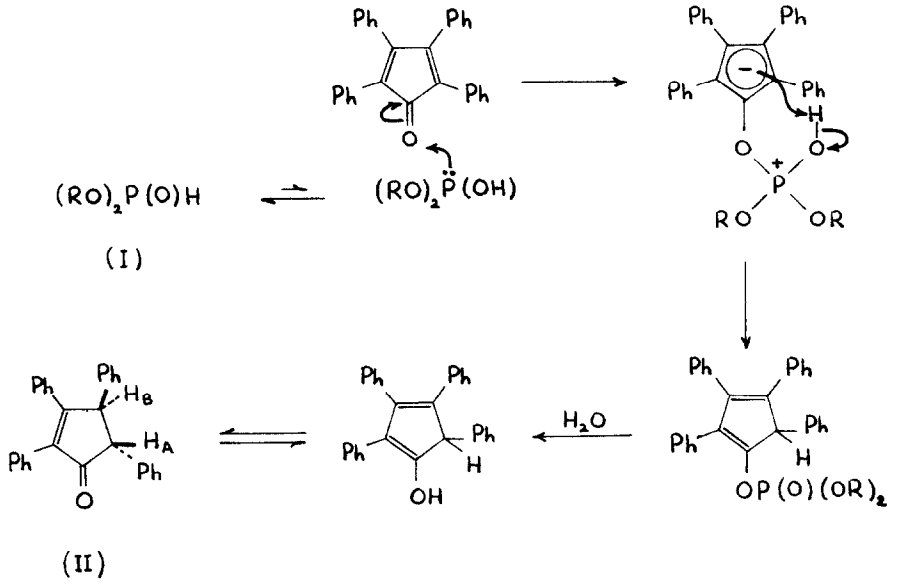
A recent publication[1] describing the reactions of tetraphenylcyclopentadienone (tetracyclone) with a variety of tervalent phosphorus compounds prompts us to record some of our own investigations in this field, which have led to new products.

Our initial interest was aroused by the observation that a solution of tetracyclone in a dialkyl hydrogen phosphonate (I; R = Me, Et), containing about 10% of water, was decolourised on heating. Addition of aqueous alcohol then gave the dihydro-compound (II)[2] (in variable yield); the assignment of a trans-stereochemistry to this product, based on the magnitude of the coupling constant (J_{AB} 2.5 Hz) for the vicinal protons H_A and H_B, is in agreement with other workers.[3] A possible mechanism for the formation of the dihydro-compound (II) is shown in Scheme 1 (cf. ref. 1). It was considered that by using a trialkyl phosphite it might be possible for an alkyl group to be transferred to the five-membered ring, and indeed tetracyclone with trimethyl phosphite in dichloromethane at room-temperature for 2-3 days yielded 1,2,3,4-tetraphenylfulvene, together with a mixture of phosphates, as found by Gallagher and Jenkins.[1]

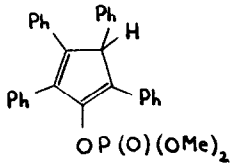
*To whom all correspondence should be addressed.



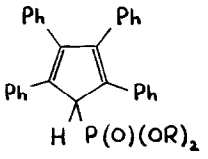
Scheme 1

However, when tetracyclone was heated under reflux with trimethyl phosphite in methanol containing 10% of water, the products included the dihydro-compound (II) (33%), 1,2,3,4-tetraphenylcyclopenta-1,3-diene[2] (5%), and an enol phosphate of m.p. 162-164° (6%) having the probable structure (III).[1] In addition, we isolated the novel phosphonate (IV; R = Me) (17%), m.p. 219-220°, the structure of which was clearly shown by its p.r.m. spectrum (60 MHz). This indicated the presence of twenty aromatic protons, one methine proton at τ 4.95 (doublet, J_{PH} 33 Hz), and six methoxy protons at τ 6.79 (doublet, J_{PH} 11 Hz). These results may be contrasted with those obtained with non-aqueous methanol as the solvent, when the reported products were the dihydro-compound (II) (60%), the phosphate (III) (10%), and the methyl ether (V) (9%).[1]

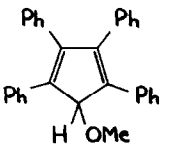
A similar reaction using triethyl phosphite in aqueous ethanol yielded the phosphonate (IV; R = Et), m.p. 197-198°, as the major product (40%); in the p.m.r. spectrum the non-aromatic protons appeared at τ 5.06 (doublet, J_{PH} 32 Hz; 1H), 6.1 - 6.8 (complex multiplet; 4H), and 9.12



(III)



(IV)



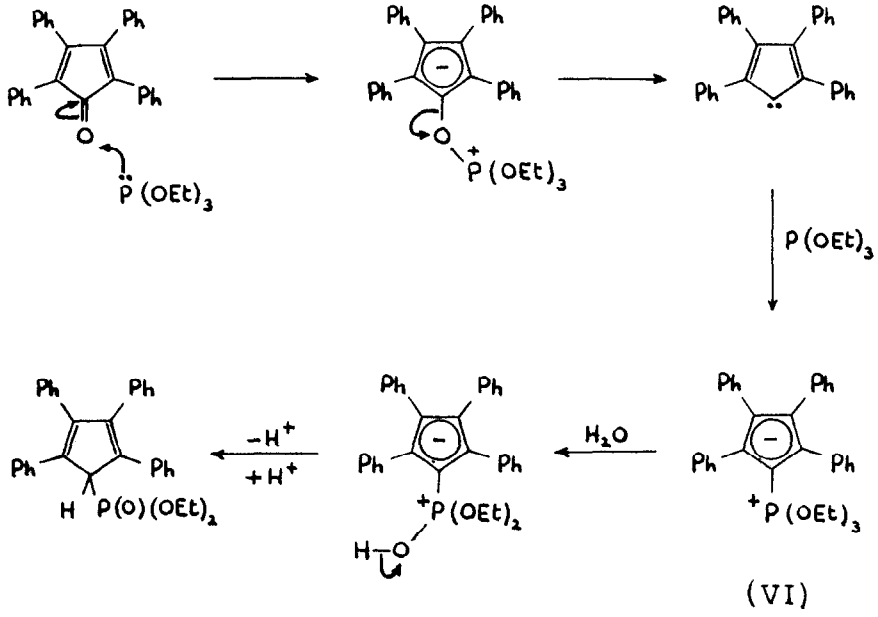
(V)

(double triplet; 6H). In this compound the geminal protons A and B in each methylene group are diastereotopic and therefore anisochronous[4] (J_{AB} 10.5 Hz), and they showed spin-coupling non-equivalence towards the phosphorus atom (J_{PA} 7, J_{PB} 9 Hz), although their couplings with the methyl protons C were indistinguishable (J_{AC} 7, J_{BC} 7, J_{PC} *ca.* 1 Hz).

The phosphonate (IV; R = Et) was accompanied by the dihydro-compound (II) (4%), and smaller quantities of two unknown phosphorus-free carbonyl-compounds, the first forming yellow prisms, m.p. 207-208° (rapid heating), and the second appearing as a white microcrystalline powder of m.p. 250.5 - 251.5° (decomp.); the structures of these last two compounds are still under investigation. Moreover, in the early stages of the reaction it was noticed that a crystalline product separated and later redissolved. This was isolated and shown to be the ylid (VI) (14%), m.p. 212-213°. The non-aromatic portion of the p.m.r. spectrum showed resonances at τ 6.26 (apparent quintet; 6H) and 9.03 (double triplet; 9H); the following coupling constants were evaluated (methylene protons labelled A, methyl protons B):- J_{AB} 7, J_{PA} 7, J_{PB} *ca.* 1 Hz.

It is of course tempting to propose a route to the phosphonate (IV; R = Et) which involves the ylid (VI) as an intermediate, and such a mechanism is outlined in Scheme 2.

Satisfactory analytical figures were obtained for the new compounds (IV; R = Me), (IV; R = Et), and (VI); unless stated otherwise, p.m.r. spectra were measured at 100 MHz in deuterochloroform.



(VI)

Scheme 2

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