Novel Insertion of the Dioxophosphorane Moiety ('Metaphosphonate') into an Aliphatic C–H Bond *via* Flash Vacuum Pyrolysis of a Cyclic Phosphonite and by Oxidation of a Diphosphene

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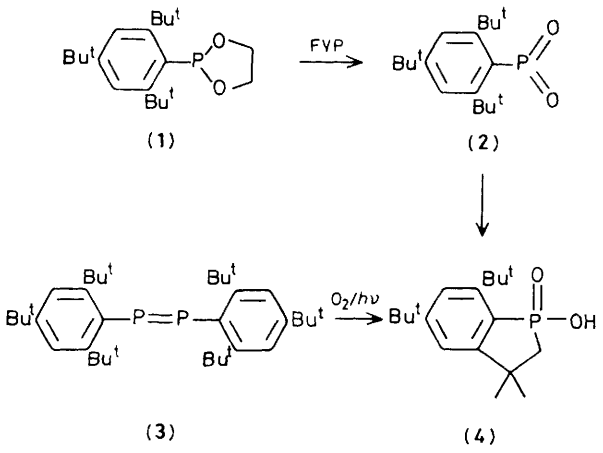
Flash vacuum pyrolysis of 2-(2,4,6-tri-t-butylphenyl)-1,3,2-dioxaphospholane (**1**) gave 5,7-di-t-butyl-3,3-dimethyl-2,3-dihydro-1-hydroxy-1λ^5-benzophosphol-1-one (**4**), 100%, also produced by photo-oxidation of bis(2,4,6-tri-t-butylphenyl)diphosphene (**3**) *via* insertion of the dioxophosphorane ($-PO_2$) moiety into a neighbouring C–H bond.

There is considerable current interest in unusually bonded phosphorus compounds, particularly in dioxophosphoranes (RPO_2)[1] and diphosphenes (RP=PR).[2] We now report novel experiments which link both species.

Thus, following the recent generation of aryldioxophosphoranes by flash vacuum pyrolysis (F.V.P.) of cyclic arylphosphonites,[3] F.V.P. at 700 °C and 0.01 mmHg of 2-(2,4,6-tri-t-butylphenyl)-1,3,2-dioxaphospholane (**1**),† prepared from 2-chloro-1,3,2-dioxaphospholane and 2,4,6-tri-t-butylphenyl-lithium by a standard route, gave the cyclic phosphinic acid (**4**) (100%, m.p. 320—323 °C) which was identical with material prepared by a different route.[4] This is the first reported example of the formal insertion of the highly electrophilic PO_2 moiety into an alkyl group and is analogous to insertion of the two-co-ordinated phosphenium ion, produced by protonation of a diaryldiphosphene,[5] also into a neighbouring t-butyl group.



(1) (2) (3) (4)

Scheme 1

† All new compounds had correct analytical and spectroscopic characteristics.

The connection with the diphosphene system is further highlighted by the novel photo-oxidation of bis(2,4,6-tri-t-butylphenyl)diphosphene (**3**)[6] which gave the same cyclic phosphinic acid (**4**) albeit in 10% yield. The reactions shown in Scheme 1 are suggested to occur with the intriguing possibility that the dioxophosphorane species (**2**) is also involved in the photo-conversion of (**3**) into (**4**).

Received, 14th September 1983; Com. 1228

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