The Chemistry of the Phosphoryl Linkage: Examples of $\mathrm{P^{IV}} \rightarrow \mathrm{P^{V}}$ and $\mathrm{P^{IV}} \rightarrow \mathrm{P^{VI}}$ Transformation under Mild Conditions

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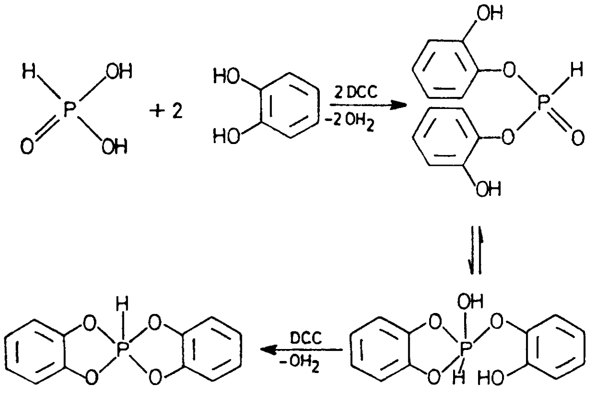
Summary Catechol and substituted catechols react with phosphonic acid or with phosphoryl chloride under mild conditions to give *P*-spirobis-(*o*-arylenedioxy)phosphoranes; where the non-cyclic substituent at phosphorus is a catechol residue the phosphoranes are readily transformed by organic bases into corresponding tris-(*o*-arylenedioxy)phosphate anions.

With very few exceptions[1] reactions of the phosphoryl group are limited to reduction to the trivalent state and require powerful reagents and/or vigorous conditions.[2] We report here reactions occurring with opening of the phosphoryl linkage which proceed under mild conditions and give rise to an increase in the co-ordination number at phosphorus.

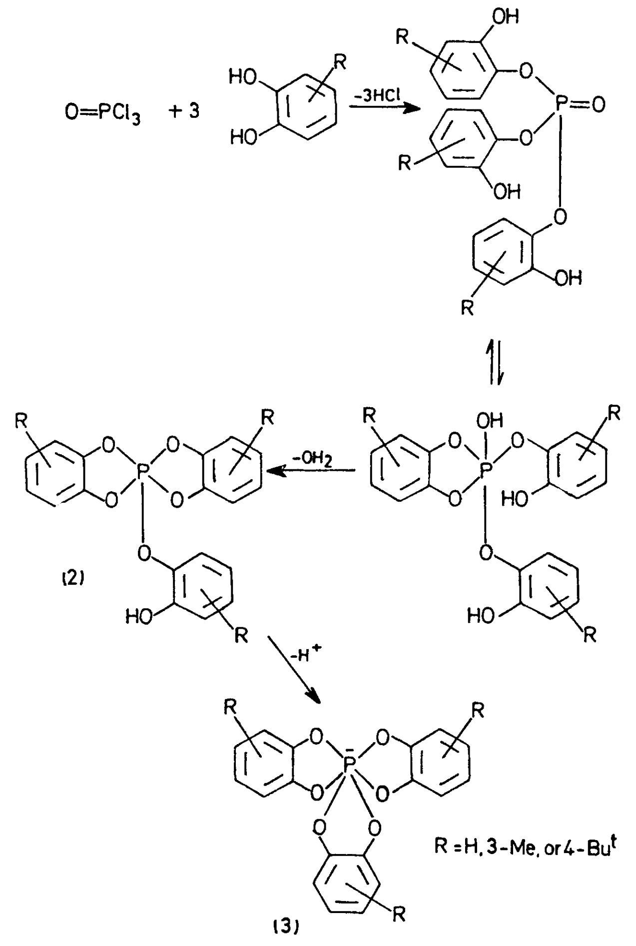
Phosphoranes are normally prepared from $\mathrm{P^{III}}$ starting materials.[2,3] However, addition of dicyclohexylcarbodiimide (DCC; 2 mol. equiv.) to a solution of anhydrous phosphonic acid (1 mol. equiv.) and catechol (2 mol. equiv.) in dry dimethoxyethane results in an exothermic



(1)

Scheme 1

reaction and the formation of the spirophosphorane (**1**) in good yield (70—80%). No reaction occurs in the absence of DCC. When the catechol is replaced by [*OH*-^{2}H]catechol, < 5% (n.m.r. analysis) of the deuterium is incorporated in the final product. The most likely course of the reaction, therefore, is the formation of the diester followed by intramolecular attack on the phosphoryl bond by the phenolic hydroxy-group (Scheme 1). Any intermediate tautomerism of the type P(O)H $\rightleftharpoons$ P–OH should result in incorporation of a P–D bond in (**1**).



Scheme 2

An even simpler reaction occurs when equimolecular amounts of catechol or substituted catechols and phosphoryl chloride are boiled together in benzene. With catechol itself a crystalline precipitate of the pentaoxyphosphorane (**2**; R = H) is formed and may be isolated simply by filtration.[4] This compound is only sparingly soluble in non-basic solvents and in basic solvents is transformed completely into the tris-(*o*-phenylenedioxy)phosphate anion (**3**), first obtained by Allcock *et al.*[5] as its triethylammonium salt. When the starting catechol is substituted (3-Me or 4-Bu^t) the intermediate phosphorane (**2**) is sufficiently soluble in non-basic solvents (benzene, acetonitrile) for ^{31}P n.m.r. measurements and the characteristic high-field absorption is consistent with a five-co-ordinated organophosphorus compound [R = 3-Me; δ (C_6H_6) −29·5 p.p.m.; R = Bu^t; δ (MeCN) −28·5 p.p.m.†]. Addition of Et_3N to these solutions causes conversion into the corresponding oxyphosphate anions (**3**) [δ(^{31}P) −83 and −84 p.p.m. respectively].

The importance of these observations lies in the fact that simple reagents and mild conditions can give good yields of products arising from reaction of the phosphoryl group. The only driving force seem to be the formation of a five-membered ring, a matter of great significance in view of the high reactivity and biological importance of naturally occurring 2,2-dioxo-1,3,2-dioxaphospholans. These observations lend strong support to the involvement of phosphoranes in the chemistry of these substances[6] and imply the possibility that such intermediate may have considerable lifetimes. In fact, there is no *a priori* reason why phosphoranes or oxyphosphate anions should not occur in nature.

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† Shifts upfield of 85% H_3PO_4 (δ = 0 p.p.m.) are denoted negative (*cf.* G. Vael, 'Annual Reports on N.m.r. Spectroscopy,' ed. E. F. Mooney, Academic Press, New York, 1973).

[1] D. Hellwinkel, *Angew. Chem.*, 1974, **13**, 542; T. Koizumi, U. Watanabe, Y. Yoshida, and E. Yoshii, *Tetrahedron Letters*, 1974, 1075; Y. Segall, I. Granoth, A. Kalir, and E. D. Bergmann, *J.C.S. Chem. Comm.*, 1975, 399.

[2] For a recent review see L. Maier, in 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, ch. 1.

[3] A. Munoz, M. Sanchez, M. Koenig, and R. Wolf, *Bull. Soc. chim. France*, 1974, 2198, and references therein.

[4] H. Gross and J. Gloede (Institut für Organische Chemie der Deutschen Akademie der Wissenschaften, Berlin-Aldershof), have submitted for publication (*Tetrahedron letters*) a paper giving details of some preparations of compound (**2**) including the reaction between phosphoryl chloride and catechol (personal communication).

[5] H. R. Allcock, R. L. Kugel, and G. Y. Moore, *Inorg. Chem.*, 1975, **14**, 2831, and references therein.

[6] F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.