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STABLE 1,4,2-DIOXAPHOSPHOLANIUM SALTS

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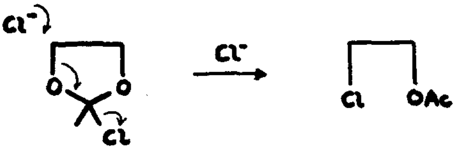
ALKOXYPHOSPHONIUM salts have long been postulated as reactive intermediates in organophosphorus reactions,[1] but only relatively recently have examples of their isolation and studies of their reactivity confirmed[2] this view. We wish to report that the reaction of benzaldehyde with monochlorophosphines leads to the 1,4,2-dioxaphospholanium chlorides (1). These salts are unique, in that they have an alkoxy ligand incorporated into a strained heterocyclic ring, and their stability is of considerable interest. Moreover, their properties allow a rationalisation of the thermal reaction between aldehydes and chlorophosphines.

In a typical preparation, benzaldehyde (2 moles) and a monochlorophosphine (2), (1 mole) are reacted, either neat or in solvent, to give a high yield of a crystalline product, to which we assign structure (1) on the basis of chemical and physical evidence. The stoichiometry of the reaction suggests that (1) is a 2:1 adduct, and this was confirmed by the hydrolysis of (1a) to an equimolar mixture of benzaldehyde and α-hydroxybenzyldiphenylphosphine oxide (3). Provided that they are kept in a moisture-free atmosphere, these salts remain stable and crystalline during storage.

The main evidence for structure (1) comes from n.m.r. studies in deuterochloroform. Of particular relevance are the ^{31}P n.m.r. shifts[‡], which are always downfield from 85% phosphoric acid [at -28.5 p.p.m. for (1a) and at -56.5 p.p.m. for (1b)], and therefore indicate[3] a phosphonium structure. This evidence rules out[3] a phosphorane structure such as (4), which might have been expected on grounds of precedent.[4] Moreover, the salts (1) show no tendency to convert to phosphoranes in favourable circumstances, even when a spirophosphorane would result, as with (1b). The ^{1}H n.m.r. spectra of (1) show two non-aromatic absorptions, each integrating for one hydrogen, which we assign to the hydrogens at C-5 and C-3 respectively. In the adduct (1a) these bands occur at τ 3.4 ($J < 1$Hz) and τ 3.9 (J 8.5 Hz), while in (1b) they appear at τ 3.6 ($J < 1$Hz), and τ 4.3 ($J < 1$Hz). These absorptions could, however, be compatible with an equimolar mixture of the <u>cis</u>- and <u>trans</u>- isomers of the related 1,3,2-dioxaphospholanium salts (5), the phosphorane analogues of which have several precedents[4] in the literature. This possibility can be discounted on the basis of the ^{13}C n.m.r. spectra[‡] of (1). For example, in the adduct (1b), the five-membered ring carbons absorb at 93.7 p.p.m. (C-5, $^{1}J_{^{31}P-^{13}C}$ 10.4 Hz) and 76.4 (C-3, $^{2}J_{^{31}P-^{13}C}$ 36.9 Hz). The ^{31}P-^{13}C coupling constants are typical of coupling over one and two bonds respectively, and are in general agreement with published work[5] on coupling in strained phosphorus heterocyclic rings. The corresponding coupling constants of (1a) (12Hz and 87.4 Hz) show this trend even more clearly.

Heating of the salts (1) converts them into α-chloroalkylphosphine oxides (6) and benzaldehyde, via the α-chloroethers (7), as outlined in the scheme. The formation of the intermediate ethers (7) is the result of an Arbusov-type dealkylation.[1,2] The subsequent transformation into the oxides (6) appears to resemble the known fragmentation of 2-chloro-1,3-dioxolanes (8)[6], or of bis-α-chlorobenzyl ether (9)[7].



(8)

$$(PhCHCl)_2O \longrightarrow PhCHCl_2 + PhCHO$$

(9)

This reaction sequence provides a rationalisation of the hitherto unexplained[8] general reaction of aldehydes with monochlorophosphines. The pathway to the phosphoryl compounds (6) is very different from that observed with phosphorus trihalides, which react as electrophiles towards aldehydes.[7] A related dependence of reaction product upon reactant structure is shown by the reactions of simple ketones with chlorodiethylphosphine[9] and with dichloro(ethyl)phosphine.[10] The factors which contribute to the unexpected stability of the salts (1), and which determine the initial role of the phosphines in these reactions, are under further study.

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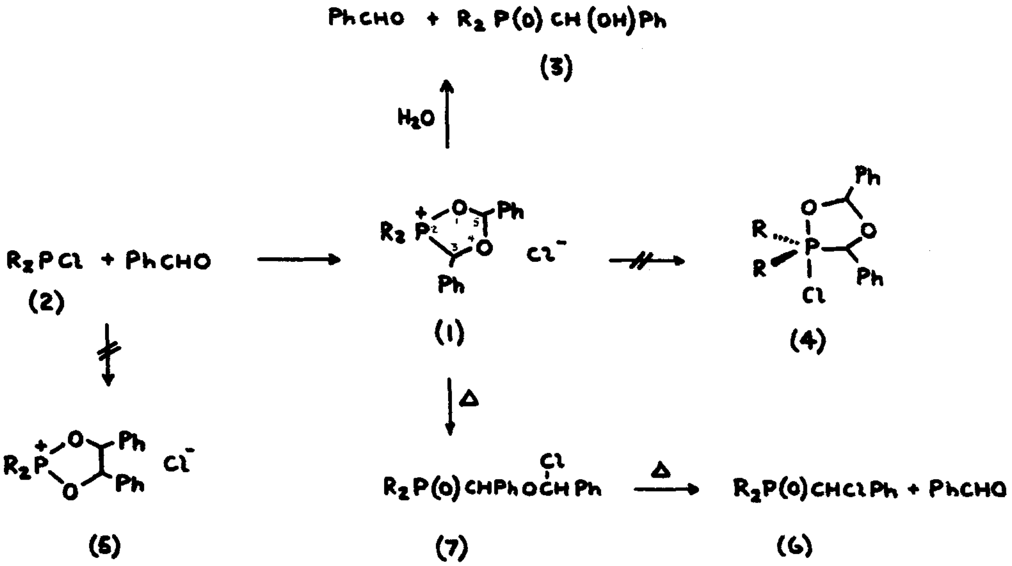

<u>SCHEME</u> Formation and reactions of 1,4,2-dioxaphospholanium salts (1). For all formulae, (a) $R_2 = Ph_2$; (b) $R_2 = -CMe_2CH_2CMe_2-$.

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