Stable Acyloxy-chlorophosphorane obtained from 2-(Diphenylphosphinyl)-benzoic Acid and Thionyl Chloride

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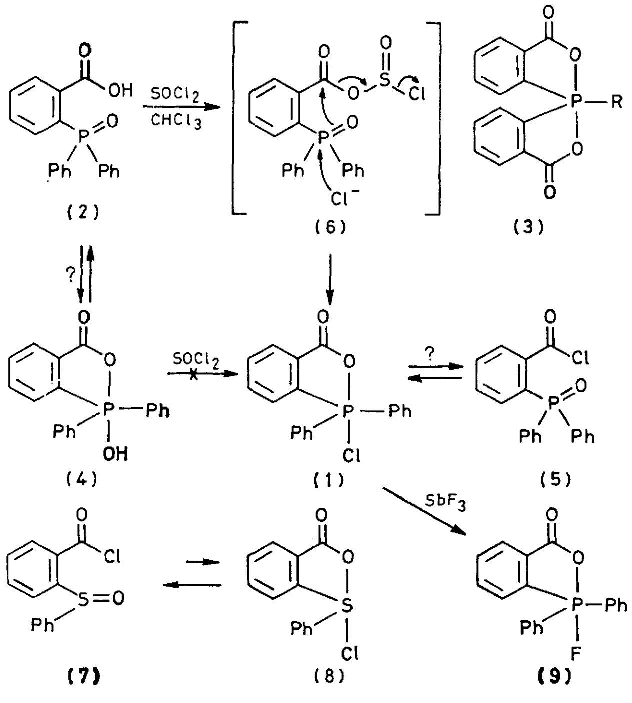
Summary The title reaction gives the novel acyloxy-chlorophosphorane (**1**) and the analogous fluoride (**9**) is similarly obtained.

The pentaco-ordinate phosphorane (**1**) is spontaneously formed from the tetraco-ordinate phosphine oxide (**2**) and thionyl chloride in chloroform. This is the first example of a surprisingly stable acyloxy-chlorophosphorane. The facile formation of compound (**1**) may be related to displacements at the tetraco-ordinate phosphorus atom which involve intermediate pentaco-ordinate species.[1] Monocyclic acyloxyphosphoranes have been postulated as intermediates in the hydrolysis of phosphoenolpyruvate esters.[2]

The intriguing preparation[3] of the exceptionally stable spirobicyclic diacyloxyphosphoranes (**3**) from bis-*o*-carboxyphenylphosphine oxides suggested to us that other facile conversions of phosphine oxides into phosphoranes may be possible.[4] Exploration of the possible nucleophilic attack by a phosphine oxide oxygen at a carbonyl group[3,5] and of the equilibria[4] of tautomers with different phosphorus co-ordination numbers is further encouraged by reports of analogous possibilities in the chemistry of sulphur compounds.[6,7]

P-Chloro-*PP*-diphenyl-2,3-benzoxaphospholen-1-one (**1**), m.p. 90—92 °C, was characterized by its ^{31}P n.m.r. chemical shift δ_P − 30·4 p.p.m. ($CHCl_3$) (from 85% H_3PO_4), a typical ^{1}H n.m.r. low-field multiplet, δ_H 9·00—9·40, assigned to the



Scheme

proton *ortho* to phosphorus in the condensed benzene ring,[8] the i.r. ν_{CO} ($CHCl_3$) 1710 cm^{-1} band associated with the cyclic acyloxy-carbonyl group[3,6] and no 1780 cm^{-1} band (*i.e.*, no acid chloride group), and the MH^+ pseudomolecular ions, *m/z* 341 and 343, in the chemical-ionization mass spectrum of compound (**1**). This spectroscopic evidence excludes the open-chain tautomeric structure (**5**) and a possible ionic phosphonium chloride-type species. The ^{31}P n.m.r. chemical-shift value of a triarylphosphine oxide, such as (**5**), should be *ca.* 70 p.p.m. down-field from that of compound (**1**). In contrast with (**1**), the analogous sulphurane (**8**) is less stable[6] than its open-chain tautomer 2-(phenylsulphinyl)benzoyl chloride (**7**) (ν_{CO} 1792 cm^{-1}).

The hydroxyphosphorane (**4**) or mixed anhydride (**6**) may be involved in the formation of compound (**1**) from (**2**). No evidence for an equilibrium between compounds (**2**) and (**4**) could be found either by spectroscopy or chemical reactivity. Compound (**2**), when heated, with *e.g.* acetic anhydride, did not yield a detectable amount of the acetyl derivative of (**4**). Moreover, the two known, stable phosphoranes[3,4a] do not react with thionyl chloride. These observations lead us to suggest that P=O oxygen attack at the carbon of the C=O group of compound (**6**) is a key step in the formation of compound (**1**) (Scheme). The intermediate (**6**) is consistent with that postulated for reactions of carboxylic acids with thionyl chloride.

The phosphorane (**1**) reacts very rapidly with water, diethylamine, or ethanol to yield tetraco-ordinate phosphorus compounds. Antimony trifluoride and compound (**1**), or thionyl fluoride and compound (**2**), give the fluorophosphorane (**9**), δ_P − 50·7 ($^1J_{PF}$ 700 Hz) p.p.m.. This relatively small $^1J_{PF}$ value is typical of an apical fluorine in a trigonal bipyramidal structure of a phosphorane as shown for (**9**). The preparation of compound (**9**) from (**1**) can be cited as an additional line of evidence for the structure of the phosphorane (**1**).

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