Sixco-ordinated Phosphorus Compounds with Three Different Bidentate Ligands

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Summary By three distinct synthetic steps, three different bidentate oxygen ligands were introduced on a central phosphorus atom.

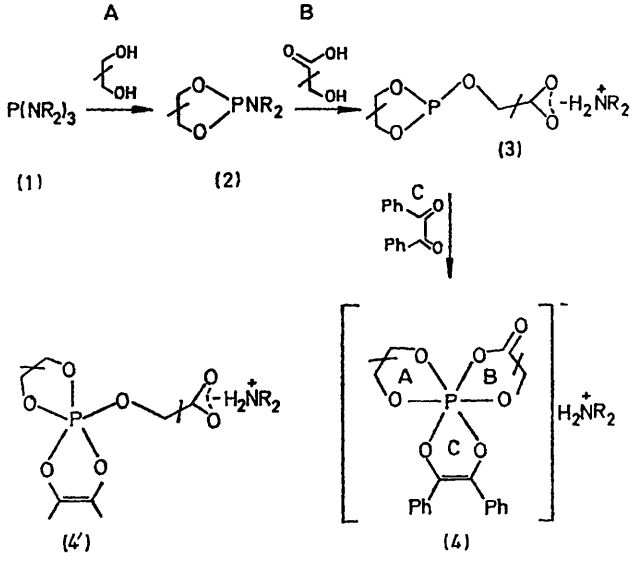
IN spite of the increasing number of papers referring to sixco-ordinated phosphorus compounds,[1] less than a hundred of the compounds have been reported.[2] Several have been prepared in which three unsaturated five-membered rings are bound to phosphorus, e.g. the tris catecholate has been isolated and characterized.[3] The first aliphatic sixco-ordinated phosphorus compound was described recently.[4]

In connection with our work on α-hydroxy-acids[5] we report here the first example in which three different ligands are successively connected to phosphorus.

TABLE

Compounds	A	B	C	R	$\delta^{31}P$ in p.p.m.[a]
(4a)	ethylene glycol	mandelic acid	benzil	Et	+93
(4b)	ethylene glycol	acetonic acid[b]	benzil	Et	+95
(4c)	pinacol	acetonic acid	benzil	Me	+97

[a] Ref.: H_3PO_4 (85%). [b] 2-Hydroxy-2-methylpropionic acid.



Compound (2) [prepared from trisdialkylaminophosphine (1) and a glycol], was treated with an α-hydroxyacid (acetonic and mandelic acid) under the previously described conditions[5] to give (3). In benzene solution, at room temperature, under nitrogen, (3) reacts like a phosphite with an α-dicarbonyl derivative to yield (4); compounds (4a), (4b), and (4c) were isolated and purified and gave satisfactory analytical data.

The n.m.r. spectra (60 MHz), in DMSO, show the presence of three different ligands A, B, and C (Table).

The i.r. spectra show ν_{CO} at 1735 cm^{-1} in CCl_4 for (4a) and (4b) and ν_{CO} at 1755 cm^{-1} in CH_2Cl_2 for (4c).

The structural assignment (4) and (or) (4') was obtained from ^{31}P n.m.r. The chemical shift values for (4a), (4b), (4c) rule out the existence of these compounds as fiveco-ordinated structures (4') for which δ values around +36 p.p.m.[6] would be expected, but are in the region reported for sixco-ordinated structures. Under the reported conditions, no evidence for the equilibrium (4) ⇌ (4') could be observed.

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