Novel Hexaco-ordinate Phosphorus Compound, Sodium Tris[ethylene glycolato(2—)]phosphate(1—)

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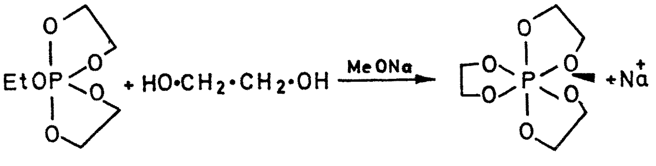
Summary Sodium tris[ethylene glycolato(2—)]phosphate-(1—) has been prepared and some of its physical and chemical properties have been determined.

HEXACO-ORDINATE phosphorus compounds are relatively rare, the major examples being the hexahalides. A series of hexa-aryl compounds have been prepared in which three five-membered rings are bonded to phosphorus.[1] More recently a tris-catecholate has been prepared and characterized.[2,3] To date no aliphatic hexaco-ordinated phosphorus compound has been reported.

Treatment of (I)[4] with ethylene glycol (1 mol. equiv.) followed by addition of NaOMe (1 mol. equiv.) gives a crystalline precipitate which has been assigned the structure (II) on the basis of the following evidence. The material shows one ^{31}P n.m.r. absorption at +89 p.p.m. relative to 85% phosphoric acid. Hellwinkel reports +82 p.p.m. for the tris-catecholate.[3] The ^{13}C 'white-noise decoupled' n.m.r. spectrum shows one absorption at +59 p.p.m. relative to Me_4Si. All the carbon atoms of (II) are equivalent and thus a single absorption is predicted provided that the P–OC coupling is small. The ^{1}H n.m.r. spectrum is complex, as expected for the AA′BB′X system in (II). A calculated spectrum using $\nu_A - \nu_B = 8{\cdot}4$, $J_{POCH} = 17{\cdot}4$ and $10{\cdot}7$, $J_{AB} = 7{\cdot}6$, $J_{AA'} = 4{\cdot}4$, $J_{BB'} = 4{\cdot}5$, and $J_{AB'} = 5{\cdot}8$ Hz duplicated the observed spectrum with a r.m.s. error of 0·15 Hz.



(I) (II)

The compound does not melt but rather decomposes at *ca.* 300—310° to give a gas and a white residue. Treatment of a methanolic solution of (II) with water causes immediate disappearance of the +89 p.p.m. absorption with the appearance of an absorption at +2 p.p.m. which is typical of phosphates. These and satisfactory analytical data, strongly support the structural assignment and thus (II) is the first aliphatic hexaco-ordinated phosphorus compound.

Attempts to prepare other hexaco-ordinated phosphorus compounds have not been nearly so successful. *E.g.*, treatment of (I) with neopentyl glycol followed by NaOMe gave mainly (II) by disproportionation. An absorption was also found at +107 p.p.m. and this may be due to a hexaco-ordinated phosphorus compound containing two five-membered rings. Similar behaviour was noted when (I) was treated with NaOMe in methanol; (II) was formed with a small amount of a material absorbing at +104 p.p.m. An attempt to prepare a six-membered ring analogue of (II) gave no evidence for its formation. These data strongly suggest that (II) has unique stability relative to other hexaco-ordinate materials.

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