

Stereochemistry of Nucleophilic Substitution at Tervalent Phosphorus.

1-Chloro-2,2,3,4,4-pentamethylphosphetan

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Summary Nucleophilic substitution on 1-chloro-2,2,3,4,4-pentamethylphosphetan occurs with inversion of configuration at phosphorus.

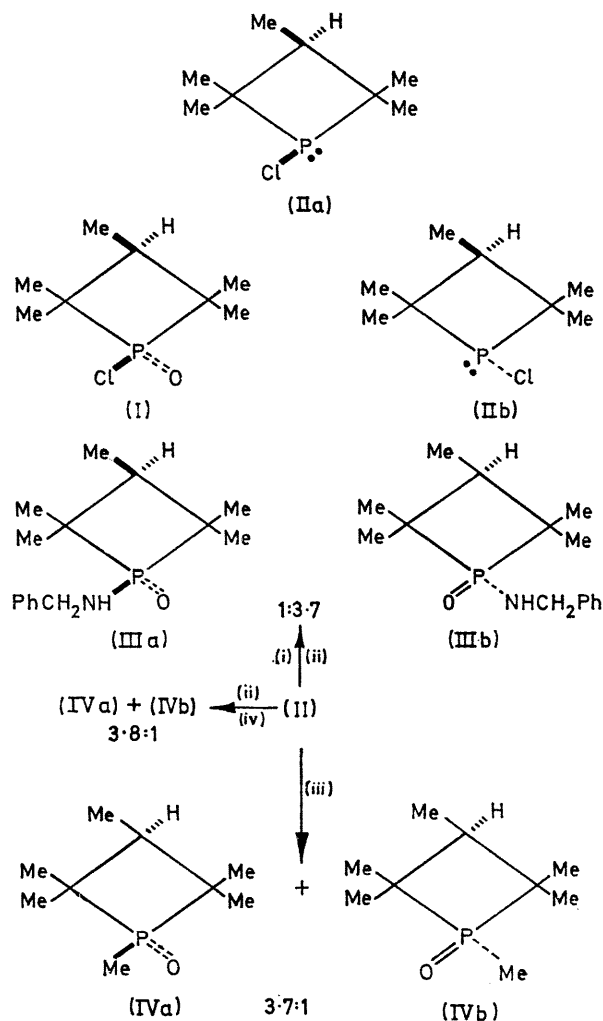
REDUCTION of the phosphinyl chloride (I) with polymethylhydrogensiloxane¹ at 120–130° gives 1-chloro-2,2,3,4,4-pentamethylphosphetan (II), b.p. 87°/20 mm. together with varying amounts of 2,2,3,4,4-pentamethylphosphetan, b.p. 32°/6 mm. The ¹H n.m.r. spectrum of (II) shows that it is a mixture of the isomers (IIa) and (IIb) and that the ratio of isomers does not change over the temperature range –50 to 125°.

Treatment of the 1-chlorophosphetan (II) with benzylamine followed by oxidation with hydrogen peroxide gives the isomeric amides (IIIa), m.p. 159–160° and (IIIb), m.p. 144–146° (total 70%) in the ratio of 1:3.7.† With sodium methoxide in methanol (II) gives the isomeric phosphine oxides (IVa) and (IVb),² formed by rearrangement of the intermediate methyl phosphinites, in the ratio 3:7:1. Oxidation of (II) with hydrogen peroxide gives > 70% of purified phosphinyl chloride (I), while treatment of the total oxidation product with methylmagnesium iodide gives the oxides (IVa) and (IVb) (total > 75%) in the ratio of 3:8:1. The phosphinyl chloride (I) is known to give only the oxide (IVa) with methylmagnesium iodide and only the amide (IIIa) with benzylamine.³

These results establish that the chlorophosphetan is a *ca.* 3:8:1 mixture of the isomers (IIa) and (IIb), and that these undergo nucleophilic substitution with predominant inversion of configuration at the phosphorus. Since the four-membered ring will occupy an apical-equatorial position in an intermediate trigonal bipyramid, these inversions may involve equatorial attack of the nucleophile and equatorial loss of the leaving group, the lone pair on phosphorus occupying an apical position.

The predominant inversion in these nucleophilic substitutions at the phosphorus of a P^{III}-phosphetan contrasts with the retention observed in similar substitutions on P^V-phosphetans.^{3,4,5}

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Reagents: (i) PhCH₂NH₂, (ii) H₂O₂, (iii) NaOMe–MeOH, (iv) MeMgI.

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† Isomer ratios were estimated by integration of the ¹H n.m.r. spectra, in deuteriochloroform solution, due to the 2,2,4,4-methyls [(IIIa) τ 8.76 and 8.84; (IIIb) τ 8.83 and 9.02 (all 3H, d, J_{PH} 17.5 Hz.)] in the total crude products.

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³ W. Hawes and S. Trippett, *J. Chem. Soc. (C)*, in the press.

⁴ W. Hawes and S. Trippett, *Chem. Comm.*, 1968, 295.

⁵ J. R. Corfield, J. R. Shutt, and S. Trippett, *Chem. Comm.*, 1969, 789.