A Two-ring Assembly Phosphazene

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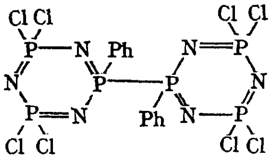
THE first ring-assembly of two phosphazene skeletons is described.

When hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (I), is treated with phenylmagnesium bromide in a variety of solvents, the main products are fully phenylated acyclic phosphazene derivatives, together with small amounts of hexaphenylcyclotriphosphazatriene, $N_3P_3Ph_6$ (II).[1,2]

By contrast, if the hexachloride (I) is allowed to react with diphenylmagnesium in refluxing dioxan, the yields of acyclic derivatives [as well as of the hexaphenyl compound (II)] are low, and a number of complex cyclic phosphazenes make up the bulk of the products. The second most abundant component (7%), m.p. 250°, can be formulated on the basis of elemental analysis and molecular weight (Calc. 708, found by osmometry in 1,2-dichloroethane 695) as $N_6P_6Ph_2Cl_8$ (III). Degradative acid hydrolysis of this product (III) affords a quantitative yield of four moles of phosphoric acid, phenylphosphonic acid also being detected. The broad P=N absorption band of this compound (III), centred at 1215 cm.$^{-1}$, closely resembles in position those of related six-membered-ring compounds, $N_3P_3Cl_6$ (1218 cm.$^{-1}$), *gem*-$N_3P_3Ph_2Cl_4$ (1190, 1210 cm.$^{-1}$), $N_3P_3PhCl_4(NPPh_3)$ (1180, 1215 cm.$^{-1}$), and $N_3P_3Cl_5(NPPh_3)$ (1175, 1215 cm.$^{-1}$), but absorbs about 50 cm.$^{-1}$ on the low-frequency side of related eight-membered-ring compounds, $N_4P_4Cl_8$ (1315 cm.$^{-1}$), and *gem*-$N_4P_4Ph_4Cl_4$ (1300, 1250 cm.$^{-1}$). The ^{31}P n.m.r. spectrum of compound (III) (for which we thank Professor E. Fluck of Heidelberg University) strongly supports a cyclotriphosphazatriene structure. The mass spectrum confirms its molecular weight (mass number 704 for $N_6P_6Ph_2{}^{35}Cl_8$), and the high intensity of the base peak at mass number 352 ($N_3P_3Ph^{35}Cl_4$) shows that the molecule is built up from two symmetric halves.

We therefore suggest for compound (III) the structure bi-(2,2,4,4-tetrachloro-6-phenylcyclotriphosphazatrien-6-yl) shown.



(III)

The formation of phosphorus–phosphorus bonds has been reported in the reactions of thiophosphoryl chloride,[3] and certain aryl substituted derivatives of thiophosphoryl chloride,[4] with some aliphatic Grignard reagents. The phosphorus–phosphorus bonds in the resultant tetra-alkyldiphosphine disulphides, $Alk_2P(S)P(S)Alk_2$ are readily cleaved by halogen under mild conditions to form dialkylphosphinothioic halides, $Alk_2P(S)X$ (X = Cl or Br). Compound (III) and tetraphenyldiphosphine disulphide, $Ph_2P(S)P(S)Ph_2$,[2] are, however, unaffected by these reagents under similar conditions.

We believe compound (III) is the first two-ring assembly of phosphazene skeletons, and the first phosphazene derivative containing a phosphorus–phosphorus bond. Insofar as there is a formal structural analogy between cyclotriphosphazatrienes and benzene, compound (III) of the biphenyl type can be added to earlier styrene and divinylbenzene analogues.[5]

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