

Formation of Bicyclic Phosphazenes *via* the Reactions of Methyl- and Phenyl-magnesium Chloride with Hexachlorocyclotriphosphazene

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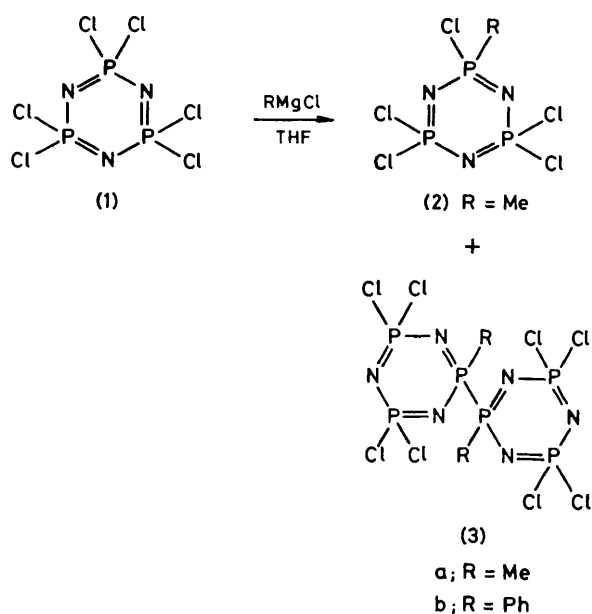
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Summary Bicyclic phosphazenes are formed in high yields when hexachlorocyclotriphosphazene reacts with organomagnesium chlorides.

THE reactions between cyclic halogenophosphazenes and organometallic reagents are exceedingly complex.¹⁻⁷ They may yield substituted cyclophosphazenes, ring-cleaved species, or traces of ring-coupled products. Ring cleavage reactions apparently predominate when hexachlorocyclotriphosphazene (**1**) reacts with phenylmagnesium bromide,⁴ diphenylmagnesium,^{5,6} or phenyl-lithium.⁷ We report here unusual results from reactions of (NPCl₂)₃ (**1**) with methyl- and phenyl-magnesium chloride in tetrahydrofuran (THF) solvent. These reactions led, not to ring-cleavage, but to the formation of well-defined products containing substituted cyclotriphosphazenes and bicyclic phosphazenes, the latter being formed in high yield.

For example, treatment of (**1**) with 2 equiv. of MeMgCl at 0 °C gave (**3a**) which was isolated in 75% yield. [³¹P n.m.r. analysis of the reaction mixture suggested virtually a 100% conversion of (**1**) into (**3a**).] At 66 °C (**3a**) was formed in 85% yield together with (**2**) (15% yield).

With phenylmagnesium chloride, the P-P linked dimer (**3b**) was formed exclusively at 0–66 °C (100% yield by ³¹P n.m.r. analysis) and was isolated in 60% yield. Both (**3a**) and (**3b**) are air-stable solids. Species (**3b**) has been reported earlier as a low yield side product from the reaction between (**1**) and diphenylmagnesium.^{5,8} Compound (**2**) was prepared in our laboratory by an alternative route from the hydridophosphazene, N₃P₃Cl₄H(Me).⁸ The formation of bicyclic phosphazenes in high yield appears to be a general reaction when primary alkylmagnesium halides react with (NPCl₂)₃; derivatives analogous to (**3a**) and (**3b**) have been isolated and characterized from reactions that involve ethyl-, n-propyl-, or n-butyl-magnesium chloride. Phenyl- and primary alkyl-magnesium bromides yielded similar products.



The structures of (**3a**) and (**3b**) were established by a combination of ³¹P n.m.r. and i.r. spectra, mass spectrometry, and microanalytical data. The proton-decoupled ³¹P n.m.r. spectra were interpreted as B₂AA'B'₂ spin systems with PCl₂ chemical shifts at 19.8 [(**3a**) and (**3b**)] and 26.4 [PPR for (**3a**)], or 17.7 p.p.m. [PPR for (**3b**)]. The organic side groups were detected by ¹H n.m.r. spectroscopy. Mass spectrometry revealed the parent ions from (**3a**) and (**3b**) and showed fragments resulting from cleavage of the molecules into two symmetrical halves.⁵ The i.r. spectrum of (**3a**) showed CH₃ bands at 2970(w), 2870(w), and 1390(w) cm⁻¹, and PN absorptions at 1280(m), 1170(s), and 1120(sh) cm⁻¹. The microanalytical data were compatible with structures (**3a**) and (**3b**).

It seems likely that compounds (3a) and (3b) are formed *via* a metal-halogen exchange-type pathway, similar to the one proposed for the formation of tetra-alkyldiphosphine disulphides.⁹ Such a mechanism would involve metallation of the cyclotriphosphazene, a process that has been well documented for hydridophosphazenes.^{10,11} Indeed, Schmidpeter and Högel¹⁰ have prepared bicyclic phosphazenes by

coupling reactions between metallocyclophosphazenes and halogenocyclophosphazenes.

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¹ C. W. Allen and P. L. Toch, *Inorg. Chem.*, 1981, **20**, 8.

² T. N. Ranganathan, S. M. Todd, and N. L. Paddock, *Inorg. Chem.*, 1973, **12**, 316.

³ M. Biddlestone and R. A. Shaw, *J. Chem. Soc. (A)*, 1970, 1750.

⁴ M. Biddlestone and R. A. Shaw, *J. Chem. Soc. (A)*, 1969, 178.

⁵ M. Biddlestone and R. A. Shaw, *Chem. Commun.*, 1968, 407.

⁶ M. Biddlestone and R. A. Shaw, *J. Chem. Soc. (A)*, 1971, 2715.

⁷ M. Biddlestone and R. A. Shaw, *Phosphorus*, 1973, **3**, 95.

⁸ H. R. Allcock and P. J. Harris, *Inorg. Chem.*, accepted for publication.

⁹ N. K. Patel and H. T. Harwood, *J. Org. Chem.*, 1967, **32**, 2999.

¹⁰ A. Schmidpeter and J. Högel, *Chem. Ber.*, 1976, **109**, 1911.

¹¹ H. R. Allcock, P. J. Harris, and R. A. Nissan, *J. Am. Chem. Soc.*, 1981, **103**, 2256.