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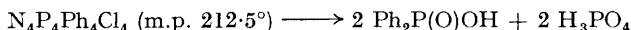
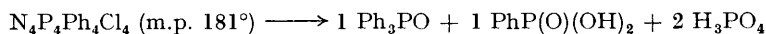
A Ring Contraction Reaction in Phosphazene Chemistry

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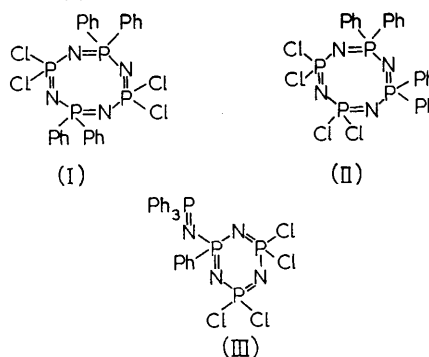
BODE and THAMER¹ reported that reaction of phenylmagnesium bromide with octachlorocyclo-tetraphosphazetene, $N_4P_4Cl_8$, yielded two isomeric tetraphenyl derivatives, $N_4P_4Ph_4Cl_4$, of m.p. 176° and 205° respectively, to which they assigned structures (I) and (II).

We have re-investigated the above system. In diethyl ether at room temperature we obtained a compound of m.p. 181° which analysed for $N_4P_4Ph_4Cl_4$. At higher temperatures ($\sim 100^\circ C$) in various solvents, or solvent mixtures, chosen from diethyl ether, toluene, and anisole, we obtained in addition a compound of identical analysis and molecular weight but of m.p. 212.5° . It seems probable that these two compounds are the same as those obtained by the earlier workers.¹ Hydrolytic degradation gave, however, entirely different results for the two compounds.



We can only reconcile the results of the hydrolytic degradation of the former with a 2,2,4,4-tetrachloro-6-phenyl-6-(2',2',2'-triphenylphosphazene-1'-yl)cyclo-triphosphazatriene, $N_3P_3Cl_4Ph(N=PPh_3)$, (III). Comparison of its infrared spectrum with those of some closely related compounds synthesised by a Kirsanov reaction from aminocyclo-triphosphazatrienes² supports the proposed structure.

From the 1H n.m.r. spectrum of the dimethyl-amino-derivative, $N_4P_4Ph_4(NMe_2)_4$, of the higher-melting compound, and the hydrolytic degradation of its chloro-precursor, we assign tentatively structure (I) to the latter.



A mechanism involving initial ring cleavage followed by cyclisation to a six-membered ring structure is compatible with the ring contraction reaction. Similar ring cleavage mechanisms with or without recyclisations may well rationalise many of the reported observations in the reactions of chlorocyclophosphazenes with organometallic reagents.³

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¹ H. Bode and R. Thamer, *Ber.*, 1943, **76B**, 121.

² R. Keat, M. C. Miller, and R. A. Shaw, *Proc. Chem. Soc.*, 1964, 137.

³ R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.