1361. *Phosphorus–Nitrogen Compounds. Part XVIII.*[1] *Further Studies on the Alkyl Halide Catalysed Rearrangements of Alkoxycyclophosphazenes*

By B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw

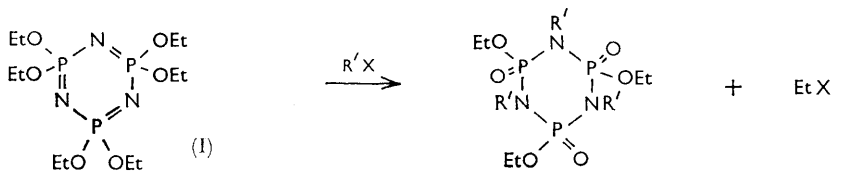
The reactions of alkoxycyclophosphazenes, $N_3P_3(OR)_6$ and $N_4P_4(OR)_8$, with alkyl halides, R′X, to give mixed oxophosphazanes, $N_3R'_3P_3O_3(OR)_3$ and $N_4R'_4P_4O_4(OR)_4$, are described. The products of such reactions provide evidence for the mechanism of the alkoxyphosphazene–oxophosphazane rearrangement. An intermediate isolated from the rection of hexaethoxycyclotriphosphazatriene with ethyl iodide has been tentatively assigned a cyclotriphosphaza-1,3-diene structure. Additional examples of such structures, and of one cyclotriphosphaz-1-ene structure, are described.

In Part VIII [2] we described the rearrangement of alkoxycyclophosphazenes, catalysed by alkyl halides. A mechanism involving nucleophilic attack by the ring nitrogen atom on the α-carbon atom of the alkyl halide was suggested.

The scope of the reaction has now been extended by the use of alkyl halides whose

[1] Part XVII, R. Keat, S. K. Roy, and R. A. Shaw, *J.*, 1965, 7193.
[2] B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J.*, 1964, 4459.

alkyl groups differ from those of the alkoxyphosphazene undergoing rearrangement. By these means we have synthesised oxophosphazanes containing mixed alkyl groups, and thereby provided support for the proposed mechanism. Thus, both isopropyl iodide and 4-nitrobenzyl bromide react with hexaethoxycyclotriphosphazatriene (I) to give the oxophosphazanes, $N_3R'_3P_3O_3(OEt)_3$ (R = Pr^i or 4-NO_2·C_6H_4·CH_2) containing three ethoxy-groups and three *N*-alkyl groups.



(I)

Evidence for the structures of these compounds is adduced from their elemental and ethoxy-group analyses, as well as from their infrared spectra [phosphoryl bands (1250 cm.$^{-1}$) [3] present, and phosphazene bands (1220 cm.$^{-1}$) [4] absent].

Because of the generation of ethyl halide in these reactions, it is necessary to employ a large excess of the reagent if a mixture of products is to be avoided. This is not so critical in the case of the reaction with 4-nitrobenzyl bromide, since the ethyl halide can be swept out of the reaction system by a stream of nitrogen. The reaction of hexamethoxycyclotriphosphazatriene with benzyl bromide gave, however, an oxophosphazane, $N_3Me(CH_2Ph)_2P_3O_3(OMe)_3$, containing only two, instead of the expected three, benzyl groups. The formation of an *N*-methyl group may result from the presence of methyl bromide (although this is not very likely, since the reaction mixture was continuously purged by a stream of nitrogen) or from the thermally promoted migration of a methyl group. That methyl groups can rearrange under these conditions (130—150°; 4 hr.) was shown by heating the hexamethoxy-derivative $N_3P_3(OMe)_6$ in boiling *m*-xylene (~140°); full rearrangement to the phosphazane $N_3Me_3P_3O_3(OMe)_3$ took place in 12 hr.

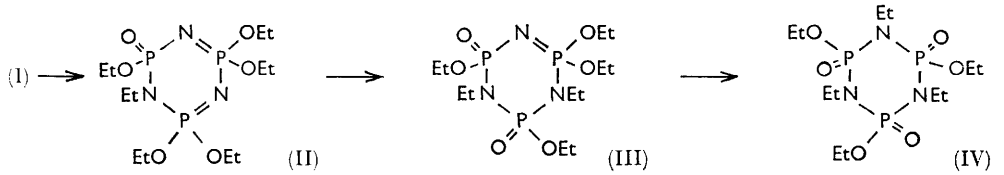
We were unable to obtain the tetrameric oxophosphazane $N_4Pr^i_4P_4O_4(OPr^i)_4$ from the reaction of octaisopropoxycyclotetraphosphazatetraene, $N_4P_4(OPr^i)_8$, with isopropyl iodide; only decomposition products and starting material could be isolated. Reaction of the same alkoxyphosphazene with methyl iodide gave, however, a mixed oxophosphazane, $N_4Me_4P_4O_4(OPr^i)_4$, and it seems likely that our lack of success in preparing the *N*-isopropyloxophosphazane is due to steric strain arising from the bulkiness of the isopropyl groups.

The expected oxophosphazane was not obtained from the reaction of hexaethoxycyclotriphosphazatriene and benzyl chloride, less than two equivalents of ethyl chloride being evolved during the reaction, and the product was shown by thin-layer chromatography to consist of two components; elemental analysis of the mixture indicated an average composition of 1·5 benzyl groups to 4·5 ethyl groups. A compound possessing a partially rearranged structure of the types probably present in the product of the benzyl chloride reaction described above was isolated on boiling hexaethoxycyclotriphosphazatriene under reflux with an excess of ethyl iodide for 1 week. This product, whose infrared spectrum showed the presence of both phosphoryl (1250 cm.$^{-1}$) [3] and phosphazene (1220 cm.$^{-1}$) [4] linkages, could be thermally rearranged to 2,4,6-triethoxy-1,3,5-triethyl-2,4,6-trioxocyclotriphosphazane. The compound is thus undoubtedly an intermediate in the rearrangement. We have some evidence that this compound is the first partial rearrangement product, 2,2,4,4,6-pentaethoxy-5-ethyl-6-oxocyclotriphospha-1,3-diene (II). (The nomenclature of cyclotriphosphazadienes and cyclotriphosphazenes is not necessarily meant to imply localised multiple bonding.)

[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1959, p. 312.

[4] L. W. Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403; R. A. Shaw, *Chem. and Ind.*, 1959, 54.

The evidence consists of the partially rearranged compound reacting with isopropyl iodide to give a product which has an infrared spectrum characteristic of an oxophosphazane, and an analysis indicating the composition $N_3EtPr^i_2P_3O_3(OEt)_3$. Additional evidence comes from experiments in which hexaethoxycyclotriphosphazatriene (I)



and ethyl iodide were heated at 170° in sealed tubes for periods varying from 15 min. to 3 hr., the reaction being followed by thin-layer chromatography. This revealed the presence of two intermediates, one being present in traces, the other having the same R_F value as compound (II). From the relative order of appearance and disappearance (see Experimental section), the latter intermediate was assigned the cyclotriphosphaza-1,3-diene structure (II).

Cyclotriphosphaza-1,3-dienes had previously only been observed for hydrolysis products where the tautomeric hydroxyphosphazene–oxophosphazane shift >P(OH)=N– ⟶ >P(=O)–NH– had taken place.[5]

One example of a cyclotriphosphaz-1-ene structure has also been observed. Hexamethoxycyclotriphosphazatriene reacts with anhydrous hydrogen chloride to give 2,2,4,6-tetramethoxy-4,6-dioxocyclotriphosphaz-1-ene, $N_3H_2P_3O_2(OMe)_4$. The infrared spectrum of this compound shows characteristic bands at 2700 (hydrogen-bonded N–H),[6] 1280 (phosphoryl),[3] and 1240 cm.$^{-1}$ (phosphazene).[4] The failure of the reaction to proceed to the oxophosphazane is presumably due to the insolubility of the intermediate. A monomeric model for this type of reaction has been reported.[7]

$$(EtO)_3P{=}NPh \xrightarrow{HCl} (EtO)_2P(:O)\cdot NHPh$$

Analogues of these novel, partially rearranged structures can be found in the dialkoxypyrimidines, where mixed *ON*-esters can be prepared by reactions with alkyl halides.[8] Mixed partially rearranged esters have been reported in the trialkoxy-1,3,5-triazines,[9] but their existence has been questioned.[10,11]

Experimental

2,4,6-*Triethoxy*-1,3,5-*tri*-4′-*nitrobenzyl*-2,4,6-*trioxocyclotriphosphazane*.—Hexaethoxycyclotriphosphazatriene (4·77 g., 0·012 mole) and 4-nitrobenzyl bromide (7·6 g., 0·036 mole) were heated together, the reaction mixture being purged by a stream of nitrogen. Evolution of ethyl bromide commenced near 115°, and the temperature of the mixture was raised during 2 hr. to 170°, at which stage reaction had ceased. The product was extracted with chloroform, and the solution was passed down a short alumina column. The solvent was removed, and the residue crystallised on standing. Recrystallisation from ethanol gave pale yellow crystals of the *product*, m. p. 168—169° (3·8 g., 44%) (Found: C, 44·6; H, 4·7; N, 11·6; P, 12·9; OEt, 19·1. $C_{27}H_{33}N_6O_{12}P_3$ requires C, 44·7; H, 4·6; N, 11·6; P, 12·8; OEt, 18·6%).

2,4,6-*Triethoxy*-1,3,5-*tri*-*isopropyl*-2,4,6-*trioxocyclotriphosphazane*.—Hexaethoxycyclotriphosphazatriene (5·0 g., 0·0124 mole) and isopropyl iodide (31 g., 0·185 mole) were heated together in a sealed tube at 170° for 55 min. The oil remaining after removal of the alkyl

[5] B. W. Fitzsimmons, C. Hewlett, K. Hills, and R. A. Shaw, unpublished results.
[6] A. D. Cross, " Introduction to Practical Infra-Red Spectroscopy," Butterworths, London, 1960, p. 65.
[7] M. I. Kabachnik and V. A. Gilyarov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, 790.
[8] G. E. Hilbert and T. B. Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 2001.
[9] A. Hantzsch and H. Bauer, *Ber.*, 1905, **38**, 1006; A. Hantzsch, *Z. anorg. Chem.*, 1932, **209**, 213.
[10] E. M. Smolin and L. Rapoport, " s-Triazines and Derivatives," Interscience, New York, 1959, p. 75.
[11] N. V. Sidgwick " The Organic Chemistry of Nitrogen," 2nd edn., Clarendon Press, Oxford, 1942, p. 344.

iodides from the mixture was dissolved in benzene and passed down a short charcoal column. The solvent was distilled off and the residue purified by short-path distillation (130°/0·01 mm.). Crystals collected on the cold-finger, and three recrystallisations from light petroleum (b. p. 60—80°) gave the *product*, m. p. 150—152° (1·78 g., 33%) (Found: C, 39·4; H, 7·5; N, 9·1. $C_{15}H_{36}N_3O_6P_3$ requires C, 40·2; H, 8·0; N, 9·4%).

1,3-*Dibenzyl*-2,4,6-*trimethoxy*-5-*methyl*-2,4,6-*trioxocyclotriphosphazane*. — Hexamethoxycyclotriphosphazatriene (4·95 g., 0·016 mole) and benzyl bromide (15·7 g., 0·091 mole) were heated together under dry nitrogen at 130—150° for 4 hr. Methyl bromide (2·1 ml., 0·038 mole) was evolved during the reaction. Unreacted benzyl bromide (8·7 g., 0·051 mole) was distilled off, and the residue dissolved in benzene and passed down a short silica gel column. Removal of solvent gave the *product* as a pale yellow solid (amorphous) (4·0 g., 47%) shown by thin-layer chromatography [methanol–chloroform (1 : 19)] to be homogeneous (Found: C, 45·3; H, 5·7; N, 8·3. $C_{18}H_{26}N_3O_6P_3$ requires C, 45·5; H, 5·9; N, 8·8%).

Attempted Rearrangement of Octaisopropoxycyclotetraphosphazatetraene.—Octaisopropoxycyclotetraphosphazatetraene (1·34 g.) and an excess of isopropyl iodide (8·2 ml.) were heated together in a sealed tube at 170° for 2 hr. Extensive decomposition was observed. Isopropyl iodide was distilled off, the residue extracted with benzene, and this solution purified as before. The solvent was removed and the residue vacuum-sublimed. The crystalline product (0·25 g.) was identified by its m. p., mixed m. p., and infrared spectrum as starting material.

2,4,6,8-*Tetraisopropoxy*-1,3,5,7-*tetramethyl*-2,4,6,8-*tetraoxocyclotetraphosphazane*.—Octaisopropoxycyclotetraphosphazatetraene (1·64 g., 0·0025 mole) and methyl iodide (40 g., 0·28 mole) were heated together in a sealed tube at 170° for 30 min. After removal of the alkyl iodides from the reaction mixture, the residue was twice subjected to short-path distillation (150°/0·01 mm.), to give the *product* as a viscous oil (Found: C, 35·9; H, 7·6. $C_{12}H_{30}N_3O_6P_3$ requires C, 35·5; H, 7·4%).

Reaction of Hexaethoxycyclotriphosphazatriene with Benzyl Chloride.—Hexaethoxycyclotriphosphazatriene (5·0 g., 0·012 mole) and benzyl chloride (4·7 g., 0·037 mole) were heated together in an atmosphere of dry nitrogen. Evolution of ethyl chloride started at a bath temperature of 180°. The temperature was increased to 192° during 2 hr., and evolution of ethyl chloride (0·9 ml., 0·014 mole) continued during this time. Excess of benzyl chloride (1·6 g., 0·013 mole) was distilled off, and the residue purified by short-path distillation (150°/0·01 mm.). Thin-layer chromatography showed the presence of two components in the product; they could not be separated by fractional distillation. Elemental analysis showed the composition to be intermediate between the 1,3-diene (one benzyl group) and the 1-ene (two benzyl groups) structures (3·8 g., 63%) (Found: C, 46·3; H, 6·5; N, 8·5; P, 18·5%; *M*, 477. $C_{17}H_{32}N_3O_6P_3$ requires C, 43·7; H, 6·85; N, 9·0; P, 19·9%; *M*, 467. $C_{22}H_{34}N_3O_6P_3$ requires C, 49·9; H, 6·4; N, 7·9; P, 17·6%; *M*, 529.)

2,2,4,4,6-*Pentaethoxy*-5-*ethyl*-6-*oxocyclotriphosphaza*-1,3-*diene*.—Hexaethoxycyclotriphosphazatriene (5·0 g., 0·012 mole) and ethyl iodide (35 g., 0·23 mole) were heated together under reflux, in the absence of light, for 1 week. Ethyl iodide was then distilled off, and the residue subjected to short-path distillation. A small amount of material distilled out at a bath temperature of 55—60° (0·01 mm.), and this was shown to be starting material. The remainder distilled at 90—100°/0·01 mm., and this was further purified by short-path distillation (100°/0·01 mm.), to give the *product* (4·4 g., 88%) (Found: C, 35·6; H, 7·4; N, 10·1; P, 22·4%; *M*, 406. $C_{12}H_{30}N_3O_6P_3$ requires C, 35·6; H, 7·4; N, 10·4; P, 22·9%; *M*, 405).

Thermal Rearrangement of 2,2,4,4,6-*Pentaethoxy*-5-*ethyl*-6-*oxocyclotriphosphaza*-1,3-*diene*.—2,2,4,4,6-Pentaethoxy-5-ethyl-6-oxocyclotriphosphaza-1,3-diene (2·0 g., 0·005 mole) was heated in an open tube at 200° for 1 hr. The product solidified on cooling, and recrystallisation from light petroleum gave 2,4,6-triethoxy-1,3,5-triethyl-2,4,6-trioxocyclotriphosphazane, m. p. and mixed m. p. 74—75° (1·21 g., 60%).

2,4,6-*Triethoxy*-1-*ethyl*-3,5-*di*-*isopropyl*-2,4,6-*trioxocyclotriphosphazane*.—2,2,4,4,6-Pentaethoxy-5-ethyl-6-oxocyclotriphosphaza-1,3-diene (1·94 g., 0·0048 mole) and isopropyl iodide (17 g., 0·1 mole) were heated together in a sealed tube at 175—180° for 35 min. The alkyl iodides were distilled off, and the residue purified by two short-path distillations (130°/0·01 mm.), to give the *product* (1·68 g., 81%) (Found: C, 39·1; H, 8·6; N, 9·3%; *M*, 421. $C_{14}H_{34}N_3O_6P_3$ requires C, 38·8; H, 7·9; N, 9·7%; *M*, 433).

2,2,4,6-*Tetramethoxy*-4,6-*dioxocyclotriphosphaz*-1-*ene*.—Hexamethoxycyclotriphosphazatriene (0·1 g., 0·0003 mole) was dissolved in diethyl ether (10 ml.), and anhydrous hydrogen chloride

bubbled through the solution. A white solid was precipitated, and this was extracted with diethyl ether to remove any remaining starting material. The *product*, which was insoluble in light petroleum, benzene, diethyl ether, and acetone, and soluble in water, ethanol, and chloroform, was recrystallised from ethanol–light petroleum (1 : 4), m. p. 182° (0·08 g., 90%) (Found: C, 16·2; H, 4·7; N, 14·25; P, 31·7. $C_4H_{14}N_3O_6P_3$ requires C, 16·4; H, 4·8; N, 14·35; P, 31·7%).

Partial Rearrangement of Hexaethoxycyclotriphosphazatriene.—A series of sealed tubes containing hexaethoxycyclotriphosphazatriene and an excess of ethyl iodide were heated at 170° for periods varing from ½ to 3 hr. The contents of each tube were examined by thin-layer chromatography on Kieselgel G plates and developed with acetone. In addition to starting material [compound (I) R_F 0·95] and the oxophosphazane (IV) (R_F = 0·82), two other components (R_F 0·61 and 0·43—0·46) were noted. From their order of appearance and disappearance (see Table) they were tentatively assigned the cyclotriphosphaza-1,3-diene (II) and the cyclotriphosphaz-1-ene structures (III), respectively. After further heating, compounds (I), (II), and (III) were no longer observed in the reaction mixture, and only the oxophosphazane (IV) could be detected.

The reaction of compound (I) with ethyl iodide

Compounds and R_F values (±0·05)	Reaction time (min.) 0	15	30	45	60	75	90	105	120—180
(I) R_F ~0·95 *	+								
(II) R_F 0·61		+	+	+	+				
(III) R_F 0·43—0·46			+	+	+	+	+	+	
(IV) R_F 0·82				+	+	+	+	+	+

* This R_F value is only approximate since the spot is so close to the solvent front.

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Department of Chemistry, Birkbeck College, University of London, Malet Street, London W.C.1. [*Received July 2nd* 1965.]