854. *Phosphorus–Nitrogen Compounds. Part VIII.*[1] *The Alkoxyphosphazene–Oxophosphazane Rearrangement.**

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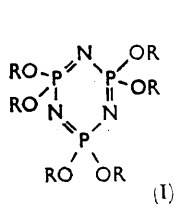
Thermal rearrangement of alkoxyphosphazenes to oxophosphazanes by $O \longrightarrow N$ alkyl migration has been observed. The scope of this reaction has been investigated, and its range extended by alkyl halide catalysis. Possible mechanisms are discussed.

In Part VII,[1] we described the preparation and some physical properties of hexa-alkoxy-(aryloxy)cyclotriphosphazatrienes (I) and of octa-alkoxy(aryloxy)cyclotetraphosphaza-tetraenes (II). During this work, rearrangement of the alkoxyphosphazene (I; R = Et) to the *N*-alkyloxophosphazane (III; R = Et) was observed to take place on heating at 200° for 1 hour.[2] The structure of the product (III; R = Et) was deduced by comparison with an authentic sample prepared by the method of Rätz and Hess.[3] In addition, degradation of the phosphazene (I; R = Et) by hydrochloric acid gave ammonia, whilst similar treatment of compound (III; R = Et) gave ethylamine. Finally, a comparison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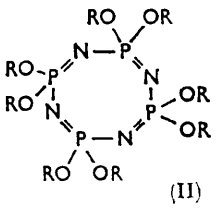
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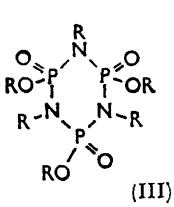
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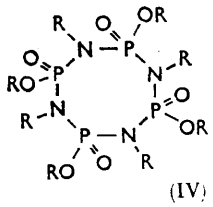
(IV)

of the infrared spectra of the two compounds revealed differences compatible with this isomerisation. The $\geqslant P{=}N{-}$ band[1,4] at 1225 cm.$^{-1}$ in the spectrum of the phosphazene

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[1] Part VII, Fitzsimmons and Shaw, *J.*, 1964, 1735.
[2] Fitzsimmons and Shaw, *Proc. Chem. Soc.*, 1961, 258.
[3] Rätz and Hess, *Chem. Ber.*, 1951, **84**, 889.
[4] Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403; Shaw, *Chem. and Ind.*, 1959, 54.

(I; R = Et) disappears, and a band at 1250 cm.$^{-1}$ ($\geqslant$P=O stretch) [5] is present in the spectrum of the product (III; R = Et) together with a doublet near 700 cm.$^{-1}$ which we provisionally assign to a P–N vibration. In extending these results to the eight-membered ring compound we found an analogous system. The phosphazene (II; R = Et) rearranged to the phosphazane (IV; R = Et) after 4 hours' heating at 200°, and the $\geqslant$P=N– band present at 1310 cm.$^{-1}$ in the spectrum of compound (II; R = Et) disappeared and was replaced by phosphoryl absorption at 1250 cm.$^{-1}$ and a doublet near 700 cm.$^{-1}$. Degradation as before gave ammonia and ethylamine, respectively.

These results provided a starting point for a systematic investigation into the scope of the rearrangement. For this investigation, some mechanistic model was required. From general principles of phosphorus chemistry, we choose one involving attack by the ring nitrogen atom on the α-carbon atom of the alkoxyl group. Such a mechanism could proceed either inter- or intra-molecularly. No distinction has so far been possible, and for the moment we depict it intramolecularly as shown (R = CH_2R'):

That α-carbon atoms in phosphates are susceptible to nucleophilic attack is demonstrated by the ready quaternisation of *N*-methylmorpholine by tribenzyl phosphate.[6] The thermal decomposition of the amidate (V) to ethylaniline and diethylaniline demonstrates the point that feebly basic nitrogen atoms are able to act under suitable conditions as nucleophiles towards α-carbon atoms of alkoxyl groups attached to phosphorus (V).[7]

$$\underset{\text{(V)}}{(EtO)_2P(:O)\cdot NHPh} \xrightarrow{260^\circ} PhNEt_2\ (85\%)\ \text{and}\ PhNHEt\ (5\%)$$

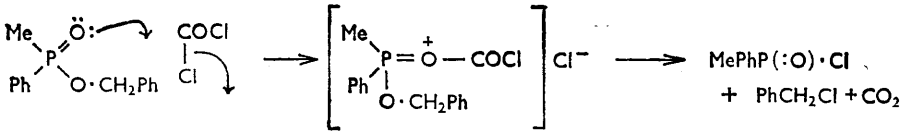
Oxygen, sulphur, or nitrogen connected to phosphorus by multiple bonds provide potential nucleophilic centres. This is well illustrated for the case of sulphur by the Pishchimuka [8] reaction:

$$(RO)_3P{=}S \xrightarrow{RI} (RO)_2P(:O)\cdot SR$$

and a number of analogous reactions involving nitrogen are known, one example being: [9]

$$(EtO)_3P{=}NPh \xrightarrow[75^\circ]{EtI} (EtO)_2P(:O)\cdot NEtPh$$

The oxygen case has been studied by Green and Hudson [10] who showed that the phosphoryl group is the nucleophile in the reaction of benzyl methylphenylphosphinate with carbonyl chloride:



In the thermal phosphazene–phosphazane rearrangement, the ring nitrogen atom behaves as the nucleophile. Quantitative evidence of the basicities of the alkoxyphosphazenes is

[5] Bellamy, " The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1959, p. 312.
[6] Baddiley, Clark, Michalski, and Todd, *J.*, 1949, 312.
[7] Cadogan, *J.*, 1957, 1079.
[8] Pishchimuka, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1406; Burn, Cadogan, and Foster, *Chem. and Ind.*, 1961, 591; Burn and Cadogan, *J.*, 1961, 5532.
[9] Kabachnik and Gilyarov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, 790.
[10] Green and Hudson, *J.*, 1963, 1004.

forthcoming from pK_a' measurements in nitrobenzene solution. Typical pK_a' values are: [11] $N_3P_3(OR)_6$; R = Et −0·2, CH_2Ph −2·1, Ph −5·8, $CH_2{\cdot}CF_3$ <−6; and $N_4P_4(OR)_8$; R = Et +0·6, CH_2Ph −1·6, Ph −6·0, $CH_2{\cdot}CF_3$ <−6.

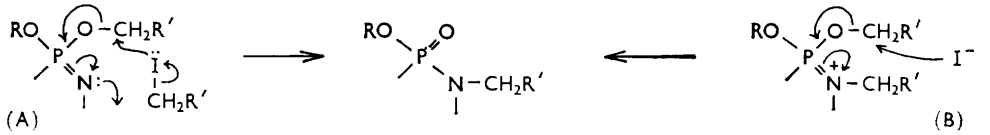
Four pieces of evidence support the mechanism proposed for the rearrangement. (*a*) The aryloxyphosphazenes (I, II; R = Ph) do not rearrange under our experimental conditions. Of the compounds we have examined, these are the most stable; they can be recovered unchanged after heating for prolonged periods at 300°. (*b*) Fluoroalkoxyphosphazenes are also exceedingly thermally stable.[12] (*c*) Hexabenzyloxycyclotriphosphazatriene undergoes rearrangement at lower temperatures and in almost quantitative yield. (*d*) Alkyl halides catalyse the rearrangement, allowing it to proceed in high yield at lower temperatures. These four points can now be considered in turn.

(*a*) In the phenoxyphosphazenes the α-carbon atom is one of an aromatic system and as such is not very susceptible to nucleophilic attack. Furthermore, the electron density at the ring nitrogen atoms is reduced relative to compounds (I, II; R = Et) (see pK_a' values). No adduct formation or rearrangement was observed when hexaphenoxycyclotriphosphazatriene was heated with ethyl iodide.

(*b*) In the case of the fluoroalkoxyphosphazenes, the electron density on the ring nitrogen atoms is lower than in the phenoxyphosphazenes; they are of at least comparable stability towards rearrangement. Thus, it appears that the lowering of the electron density on nitrogen atoms, together with the increased difficulty of breaking the oxygen–carbon bond, outweighs any activation of the α-carbon atom by the trifluoromethyl groups.

(*c*) An intermediate case is provided by one of the benzyloxyphosphazenes where activation by the phenyl group allows reaction (I) ⟶ (III) (R = CH_2Ph) to proceed at a lower temperature and in high yield. However, the system is rather complex, as we were unable to obtain a clearly defined product from the rearrangement of the phosphazene (II; R = CH_2Ph) under our conditions (see Experimental section).

(*d*) The catalysis of our rearrangement by alkyl halides bears obvious analogies to the Pishchimuka and Kabachnik reactions. Our basicity studies show the ring nitrogen atom to be the centre of greatest electron density in phosphazene molecules, and therefore we formulate the rearrangement either as a concerted attack involving a six-membered transition state (A) or as quaternary-adduct formation (B) followed by nucleophilic attack of iodide ion on the α-carbon atom:



The latter recalls the use of iodides as dealkylating agents for phosphorus esters.[13] In the above quaternary structure the α-carbon would be strongly activated towards nucleophilic attack by the positive charge on the ring which would also facilitate $\geq PO-C-$ fission. For the rather more basic aminophosphazenes [11] we have shown [14] that alkyl halide adducts are isolable, *e.g.*, $N_3P_3(NHEt)_6$,MeI.

The above mechanistic discussion is somewhat oversimplified, as no consideration was given to steric factors, and pK_a' values were taken to be a measure of nucleophilicity towards the saturated α-carbon atom. In general, the basicities of a series of compounds towards protons will not necessarily be in the same order as their nucleophilic reactivities towards

[11] Feakins, Last, Neemuchwala, and Shaw, *Chem. and Ind.*, 1963, 164; Feakins, Last, and Shaw, *ibid.*, 1962, 510; Feakins, Last, Neemuchwala, and Shaw, *J.*, to be published.
[12] Rätz, Schroeder, Ulrich, Kober, and Grundsmann, *J. Amer. Chem. Soc.*, 1962, **84**, 552.
[13] See, *e.g.*, Maruszewska-Wieczorkowska, Michalski, and Zwierzak, *Chem. and Ind.*, 1961, 1668.
[14] Das, Shaw, Smith, Last, and Wells, *Chem. and Ind.*, 1963, 866.

saturated carbon atoms. However, taking the basicity of alkoxy(aryloxy)phosphazenes as some measure of their nucleophilic reactivity towards the saturated α-carbon atoms in alkoxyphosphazenes is perhaps not seriously amiss as the compounds compared are all of the same basic structure.

Perhaps the stability towards rearrangement of the fluoroalkoxyphosphazenes is best understood by considering one further possibility, namely, that the inductive effect of the CF_3 group may hinder the departure of the oxygen atom with the bonding pair of electrons. The observation of alkyl halide catalysis for rearrangement of more basic alkoxyphosphazenes lends support to this (cf. proposed mechanisms).

Electron withdrawal from the α-carbon atom may be brought about by suitable groupings regardless of their positions relative to the carbon–oxygen bond. However, its heterolysis will be assisted if the electron sink is on the oxygen side, and hindered by electron demands on the carbon side of the bond. The effective rate will depend on the balance of these and other effects.

The thermal stability of alkoxyphosphazenes has been discussed from time to time.[15] Dishon [16] noted that compound (I; R = Me) tended to decompose partially on distillation. Probably this decomposition proceeds, at least in part, through further rearrangement of the phosphazanes.

The alkyl halide catalysed reaction is more easily controlled than the thermal one; a range of new phosphazanes, prepared by the former method, are included in the Table.

Preparation of the phosphazanes $N_3R_3P_3O_3(OR)_3$ (III) and $N_4R_4P_4O_4(OR)_4$ (IV).

Compound	M. p.	Method of preparation: Heating	Method of preparation: RI
(III; R = Me)	127—128°	*	170°/3·5 hr.
(III; R = Et)	74—75	200°/1 hr.	170°/3 hr.
(III; R = Pr^n)	21—23	—	170°/6 hr.
(III; R = Pr^i)	179—180	—	175°/0·7 hr.
(III; R = CH_2Ph)	88—89	160°/2·7 hr.	—
(IV; R = Me)	235	—	170°/3 hr.
(IV; R = Et)	208—210	200°/4 hr.	170°/4·7 hr.

* Isolated from a distillation; see Experimental section.

Experimental

Benzene, diethyl ether, and light petroleum (b. p. 60—80° unless otherwise stated) were dried over sodium wire. Alkyl halides were freshly distilled before use. Infrared spectra were measured as liquid films or using KBr discs, as appropriate, with a Perkin-Elmer Infracord spectrometer. Melting points were determined on a Reichert–Kofler micro heating stage fitted with a polarising microscope.

2,4,6-*Trimethoxy*-1,3,5-*trimethyl*-2,4,6-*trioxocyclotriphosphazane*.—(*a*) Hexamethoxycyclotriphosphazatriene (I; R = Me) (1·5 g., 4·7 mmoles) and methyl iodide (15 g., 105 mmoles) were heated together in a sealed tube at 170—175° for 3·5 hr. The unreacted methyl iodide was removed by distillation and the residue dissolved in benzene and decolourised on a short alumina column. The crystalline *product* was purified by vacuum-sublimation (120°/0·1 mm.) and recrystallised from light petroleum, to give 0·7 g. (47%), m. p. 127—127·5° (Found: C, 22·0; H, 5·4; N, 13·0; P, 29·5. $C_6H_{18}N_3O_6P_3$ requires C, 22·5; H, 5·6; N, 13·1; P, 28·9%.

(*b*) The residue from the distillation of hexamethoxycyclotriphosphazatriene (I; R = Me) was extracted with hot light petroleum (b. p. 80—100°). The solution deposited crystals of the cyclotriphosphazane, m. p. and mixed m. p. 126—127° (from light petroleum).

2,4,6-*Triethoxy*-1,3,5-*triethyl*-2,4,6-*trioxocyclotriphosphazane*.—(a) *By the thermal method.* The phosphazene (I; R = Et) (12·12 g.) was kept at 200° for 1 hr. in a flask closed with a calcium chloride guard-tube. On cooling, the crude product solidified. It was pressed on a porous tile, dissolved in benzene–light petroleum (1 : 1), and the solution passed through a short

[15] Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.
[16] Dishon. *J. Amer. Chem. Soc.*, 1949, **71**, 2251.

column of alumina. After removal of solvent, the residue was recrystallised three times from light petroleum, to give the cyclotriphosphazane (2·93 g., 29%), m. p. 74—75°, identical (mixed m. p. and infrared spectrum) with an authentic sample [3] (Found: C, 35·9; H, 7·2; N, 10·3. Calc. for $C_{12}H_{20}N_3O_6P_3$: C, 35·6; H, 7·4; N, 10·4%).

(b) *From hexaethoxycyclotriphosphazatriene and ethyl iodide.* The phosphazene (I; R = Et) (4·14 g., 10·2 mmoles) and ethyl iodide (23 g., 147 mmoles) were heated together (see Table), to give the cyclotriphosphazane (2·26 g., 56%) (m. p. and mixed m. p. 74—75°, and correct infrared spectrum).

2,4,6-*Tri-n-propoxy*-1,3,5-*tri-n-propyl*-2,4,6-*trioxocyclotriphosphazane*.—The phosphazene (I; R = Pr^n) (4·0 g., 8·2 mmoles) and n-propyl iodide (21 g., 124 mmoles) were heated together in a sealed tube at 170° for 6 hr. n-Propyl iodide was then distilled off and the residue dissolved in benzene and passed through a short charcoal column. The product, a yellow oil, was twice subjected to molecular distillation (120°/0·01 mm.) and then chromatographed (0·437 g. on 50 g. of silica gel). A colourless oil was eluted with ether–benzene (1 : 1), and this crystallised on refrigeration, to give the *product* (0·350 g., 9%) m. p. 21—23° (Found: C, 43·9; H, 8·7; N, 8·8; P, 19·3. $C_{18}H_{42}N_3O_6P_3$ requires C, 44·2; H, 8·6; N, 8·6; P, 19·0%).

2,4,6-*Tri-isopropoxy*-1,3,5-*tri-isopropyl*-2,4,6-*trioxocyclotriphosphazane*.—Hexaisopropoxycyclotriphosphazatriene (3·2 g., 6·5 mmoles) and isopropyl iodide (15·6 g., 92 mmoles) were heated together (see Table), to give the *product* (0·28 g., 10%) m. p. 179—180° (Found: C, 43·8; H, 8·6; N, 8·7; P, 19·8%).

1,3,5-*Tribenzyl*-2,4,6-*tribenzyloxy*-2,4,6-*trioxocyclotriphosphazane*.—Hexabenzyloxycyclotriphosphazatriene (1·98 g.) was kept at 160° for 2·66 hr. The solid obtained on cooling had m. p. 76—85°. One recrystallisation from benzene–light petroleum (1 : 1) gave the *product* (1·92 g., 97%), m. p. 88—89° (Found: C, 65·0; H, 5·6; N, 5·2%; *M*, 873. $C_{42}H_{42}N_3O_6P_3$ requires C, 64·9; H, 5·4; N, 5·4%; *M*, 777).

2,4,6,8-*Tetramethoxy*-1,3,5,7-*tetramethyl*-2,4,6,8-*tetraoxocyclotetraphosphazane*.—The phosphazene (II; R = Me) (5 g., 11·7 mmoles) and methyl iodide (30 g., 212 mmoles) were heated together (see Table), to give an oily solid. Vacuum-sublimation and recrystallisation from light petroleum gave the *product* (2·55 g., 50%), m. p. 235° (Found: C, 22·3; H, 5·5; N, 13·1. $C_8H_{24}N_4O_8P_4$ requires C, 22·5; H, 5·6; N, 13·1%).

2,4,6,8-*Tetraethoxy*-1,3,5,7-*tetraethyl*-2,4,6,8-*tetraoxocyclotetraphosphazane*.—(a) *By the thermal method.* The phosphazene (II; R = Et) (2·61 g.) was heated as before (Table), to give a solid. Two recrystallisations from benzene–light petroleum (1 : 1) gave the *product*, m. p. 208—210° (0·163 g., 6%) (Found: C, 35·1; H, 7·6; N, 10·6%; *M*, 507. $C_{16}H_{40}N_4O_8P_4$ requires C, 35·6; H, 7·4; N, 10·4%; *M*, 540).

(b) *From octaethoxycyclotetraphosphazatetraene and ethyl iodide.* The phosphazene (II; R = Et) (2·43 g., 4·5 mmoles) and ethyl iodide (20 g., 128 mmoles) were heated together (see Table), to give the cyclotetraphosphazane (0·25 g., 10%), m. p. 208—210°.

Acid Degradation of 2,4,6-*Triethoxy*-1,3,5-*triethyl*-2,4,6-*trioxocyclotriphosphazane*.—The compound (2·84 g.) was sealed in a tube with 10% ethanolic hydrogen chloride (25 ml.), and kept at 160° for 24 hr. The mixture was transferred to a flask (100 ml.) and the ethanol evaporated *in vacuo*. The residue was decomposed with potassium hydroxide and the liberated basic material swept out with nitrogen and trapped in ethereal hydrogen chloride. Complete decomposition was effected by gentle heating with a "cool" Bunsen flame. Ethylamine hydrochloride, m. p. 95—97° (1·06 g., 62·9%), was isolated from the ether solution.

Acid Degradation of 2,4,6,8-*Tetraethoxy*-1,3,5,7-*tetraethyl*-2,4,6,8-*tetraoxocyclotetraphosphazane*.—The compound (0·2366 g.) was treated with 10% ethanolic hydrogen chloride and then potassium hydroxide, as above. In this case, the small amount of ethylamine hydrochloride was identified by paper ionophoresis. Conventional apparatus was used and 5% aqueous solutions of ammonium and ethylammonium chloride were used as reference compounds. A field of ~3 v $cm.^{-1}$ was used in a buffer of $7·5 \times 10^{-3}$N-HCl.[17] The spots were developed with 5% ninhydrin after 2 hr. Under these conditions, ammonium and ethylammonium chloride are separated well, and in this experiment only ethylammonium chloride was detected.

Heating of Hexaphenoxycyclotriphosphazatriene and Octaphenoxycyclotetraphosphazatetraene.—The above compounds were kept at 300° for 26 hr. After this time they were recovered unchanged (m. p. and infrared spectra). Heating of hexaphenoxycyclotriphosphazatriene with ethyl iodide in a sealed tube at 200° for 3 hr. gave a similar result.

[17] Crawford and Edward, *Chem. and Ind.*, 1956, 1274.

Action of Heat on Octabenzyloxycyclotetraphosphazatetaene.—Five unsuccessful attempts were made to convert this compound into 1,3,5,7-tetrabenzyl-2,4,6,8-tetrabenzyloxy-2,4,6,8-tetraoxocyclotetraphosphazane by heating on a *ca.* 100 mg. scale as follows: 1, at 150° for 1 hr.; 2, at 150° for 2 hr.; 3, at 150° for 3 hr.; 4, at 175° for 3 hr.; 5, at 200° for 1 hr. Experiments 1—4 afforded no compound of the expected type, starting material only being recovered. Experiment 5 resulted in decomposition.

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