338. *Phosphorus–Nitrogen Compounds. Part VII.*[1] *Alkoxy- and Aryloxy-cyclophosphazenes.*

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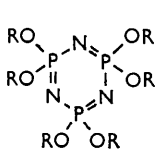
A representative series of alkoxy- and aryloxy-derivatives of cyclotriphosphazatriene, $N_3P_3(OR)_6$, and cyclotetraphosphazatetraene, $N_4P_4(OR)_8$, (R = Me, Et, Pr^n, Pr^i, Bu^n, $PhCH_2$, Ph, *p*-$MeO{\cdot}C_6H_4$, and 2-$C_{10}H_7$) have been prepared, and their properties are discussed. Chloropentaphenoxycyclotriphosphazatriene, $N_3P_3Cl(OPh)_5$, has been isolated; this is contrasted with the absence of its chloropenta-amino-analogues.

Unsuccessful investigations into reactions of chlorophosphazenes with alcohols and phenols date back to 1926. This work has been summarised.[2] Dishon [3] in 1949 prepared, from hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, the first hexa-alkoxycyclotriphosphazatrienes, $N_3P_3(OR)_6$, (I; R = Me or Bu^n). These were prepared by use of methanolic sodium

[1] Part VI, Hills and Shaw, *J.*, 1964, 130.
[2] Shaw, Fitsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.
[3] Dishon, *J. Amer. Chem. Soc.*, 1949, **71**, 2251.

methoxide and n-butanol–pyridine, respectively, and purified by vacuum distillation with considerable loss attributed to thermal instability. Later, a hexaethoxy-derivative, $N_3P_3(OEt)_6$, was described [4] as a water-soluble, viscous liquid, which decomposed at about 90° to diethyl ether and a gummy residue. More recently, octamethoxycyclotetraphosphazatetraene, $N_4P_4(OMe)_8$,[5] and some fluoroalkoxy- [6] and aryloxy-phosphazenes [7] have been reported. Other alkoxy- and aryloxy-phosphazenes described [8] lack acceptable criteria of purity such as boiling point or melting point.

We have investigated the alcoholysis and phenolysis of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, and octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, in some detail. A preliminary account of this work has appeared.[9] Two reaction routes were explored for the synthesis of hexa-alkoxy- and hexa-aryloxy-cyclotriphosphazatrienes, $N_3P_3(OR)_6$, (I)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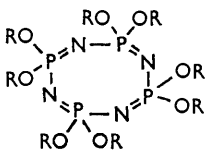
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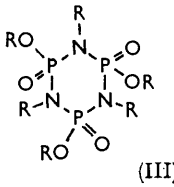
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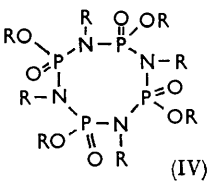
(IV)

and octa-alkoxy- and octa-aryloxy-cyclotetraphosphazatetraenes, $N_4P_4(OR)_8$, (II): (i) reaction with sodium alkoxides and aryloxides; and (ii) reaction with alcohol–pyridine mixtures. In general, we have found that the pyridine method (ii) is convenient for the synthesis of alkoxy-derivatives, as it obviates the additional step of preparing the sodium alkoxides. However, the sodium alkoxide method (i) appears to be equally satisfactory.

Reactions with primary alcohols, ROH (R = Me, Et, Pr^n, or Bu^n), proceed readily at, or below, room temperature. However, when the preparation of hexamethoxycyclotriphosphazatriene (I; R = Me) by the pyridine method was attempted, complete decomposition took place on removal of solvent and excess of pyridine prior to distillation. It is probable that at least part of this decomposition was due to nucleophilic attack of pyridine on the α-carbon atom. The pure ester, prepared by the sodium methoxide method, decomposed at about 90° in the presence of pyridine, and on one occasion we were able to isolate the methylpyridinium cation as its mercuri-iodide. In contrast to the reactions with primary alcohols, the pyridine method (ii) did not give complete replacement of chlorine by means of isopropyl alcohol at room temperature. From octachlorocyclotetraphosphazatetraene, a material was isolated by distillation, which gave an analysis for a pentaisopropoxy-derivative, $N_4P_4(OPr^i)_5Cl_3$, but no clear evidence was obtained as to its homogeneity. Complete replacement of chlorine by isopropoxy-groups was achieved by prolonged boiling of the chlorophosphazenes in isopropyl alcohol with an excess of sodium isopropoxide.

That the complete replacement of chlorine atoms by alkoxy-groups requires considerably more drastic conditions for isopropyl alcohol than with unbranched alcohols, suggests that steric factors are of importance. This parallels observations made earlier on the aminolysis of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$,[10] its phenyl-derivatives, $N_3P_3Ph_2Cl_4$ and $N_3P_3Ph_4Cl_2$,[1] and octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$.[11]

As we had earlier observed the thermal alkoxyphosphazene–oxophosphazane rearrangements [12] (I) ⟶ (III) and (II) ⟶ (IV), and as many of our derivatives were isolated by

[4] Rätz and Hess, *Chem. Ber.*, 1951, **84**, 880.
[5] Shaw, *Chem. and Ind.*, 1959, 54.
[6] Rätz, Schroeder, Ulrich, Kober, and Grundmann, *J. Amer. Chem. Soc.*, 1962, **84**, 551.
[7] Nichols; McBee and co-workers, quoted in ref. 17.
[8] Cf. Table XIII, ref. 17.
[9] Fitzsimmons and Shaw, *Chem. and Ind.*, 1961, 109.
[10] Ray and Shaw, *J.*, 1961, 872.
[11] Ray, Shaw, and Smith, *J.*, 1963, 3236.
[12] Fitzsimmons and Shaw, *Proc. Chem. Soc.*, 1961, 258.

vacuum distillation at relatively elevated temperatures, hydrolytic degradations were carried out to determine their structures. No alkylamines were detected, and ammonia was isolated in good yields as ammonium chloride, thus providing chemical evidence for the alkoxyphosphazene structures (I) and (II).

To determine why the earlier reported hexaethoxy-derivative, $N_3P_3(OEt)_6$, decomposed at a relatively low temperature to yield ether,[4] the ethoxyphosphazene was treated with sodium ethoxide, or the trisodium salt of the hydroxyoxocyclophosphazane, $(N_3H_3P_3O_6)^{3-}$ $3Na^+$ (as prototype for partially hydrolysed compounds), both conceivable catalysts for this decomposition, which might have been present owing to the method of synthesis. However, no evolution of ether was observed on heating the mixtures to 120°.

In the synthesis of the aryloxyphosphazenes, we preferred the sodium aryloxide route (i). As the direct synthesis of the reagents from sodium and phenols in benzene was slow, the aryloxides were prepared by the exchange reaction with sodium ethoxide, ArOH + NaOEt $\rightleftharpoons$ ArONa + EtOH, the ethanol being removed by fractional distillation, and replaced by anhydrous dioxan, in which the reactions were subsequently carried out. These reactions required more forcing conditions than those with alcohols, in line with general observations on the reactivity of phosphorus–chlorine bonds.[13] The aryloxyphosphazenes (I and II; R = Ph, *p*-MeO·C_6H_4, or 2-$C_{10}H_7$) were prepared and characterised.

Octaphenoxycyclotetraphosphazatetraene occurs in three modifications, having melting points 65—66, 70—71, and 85—86°. The higher-melting forms are produced on heating the lower melting forms; the infrared spectra in the region 4000—700 cm.$^{-1}$ appear to be identical. Differences in crystalline form or conformational isomerism are possible explanations. Different melting points for the same compound have been observed with other cyclophosphazene derivatives.[14] Two forms of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, corresponding to distinct conformers, have been investigated by *X*-ray diffraction.[15] Two octaphenyl derivatives have also been reported.[16]

Chloropentaphenoxycyclotriphosphazatriene, $N_3P_3Cl(OPh)_5$, can be readily prepared either by use of stoicheiometric quantities of reagent or by not forcing to completion a reaction designed to yield the hexaphenoxy-derivative, $N_3P_3(OPh)_6$. The ease with which a monochloro-derivative can be obtained in this system contrasts with the complete, or almost complete, absence of monochloro-derivatives in the aminolysis of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ [2,10] [three apparent exceptions to this are reported in a recent review: [17] one of these is due to an error, the hydrochloride of the hexa-n-butylamino-derivative, $N_3P_3(NHBu^n)_6$,HCl,[18] being mistaken for the penta-aminochloro-compound $N_3P_3Cl(NHBu^n)_5$; for the other two, secondary amine derivatives, no analytical figures or methods of preparation are given], its geminal diphenyl derivative, $N_3P_3Ph_2Cl_4$,[1] and octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$.[11] It has been suggested [1] that a possible cause for their absence is (*a*) the successful competition of the monochloro-derivatives, *e.g.*, $N_3P_3Cl(NRR')_5$, for the hydrogen chloride formed during reaction, and the thus much increased reaction rate of the protonated conjugate acid, *e.g.*, $N_3P_3Cl(NRR')_5H^+$, or (*b*) a change in mechanism, *e.g.*, an ionisation process of the remaining phosphorus–chlorine bond in the monochloro-compounds, due to the cumulative electron-releasing effect of a number of amino-substituents.

In the above synthesis of the chloropentaphenoxy-compound, protonation cannot occur, as the molecule eliminated in the replacement process is sodium chloride. Basicity measurements in nitrobenzene solution suggest that the electron supply to the ring

[13] Dostrovsky and Halmann, *J.*, 1953, 508.
[14] Shaw and Stratton, *J.*, 1962, 5004; Bullen, Shaw, and Stratton, unpublished results.
[15] Hazekamp, Migchelsen, and Vos, *Acta Cryst.*, 1962, **15**, 539; Wagner, Vos, de Boer, and Wichertjes, Sixth Internat. Congress and Symp. of the Internat. Union of Crystallography, Rome, 1963.
[16] Bode and Thamer, *Ber.*, 1943, **76**, 121.
[17] Schmulbach, *Prog. Inorg. Chem.*, 1962, **4**, 366.
[18] Ray and Shaw, *Chem. and Ind.*, 1961, 1173.

from phenoxy-groups is very much less than that from amino-groups, some relevant pK_a' values in nitrobenzene being: $N_3P_3(NMe_2)_6$, 7·6;[19] $N_3P_3(NMe_2)_4Cl_2$, −1·4;[19] $N_3P_3(NMe_2)_3Cl_3$, $\leqslant -6·0$;[19] $N_3P_3(OPh)_6$, $\leqslant -6·0$;[20] $N_3P_3Cl_6$, $\ll -6·0$.[20] Hence a change in mechanism due to a greatly increased electron supply is unlikely.

The alkoxyphosphazenes are colourless, odourless, mobile liquids, or low-melting crystalline solids, sparingly soluble or insoluble in water (the solubility decreases with increasing length of the alkyl chains), and when pure can be distilled unchanged under reduced pressure (see Experimental section). The hexamethoxy-derivative (I; R = Me), however, is appreciably soluble in water, and requires molecular rather than conventional distillation. These properties (which resemble those of the recently reported fluoroalkoxyphosphazenes)[6] are in contrast to those reported by other authors,[4,6,16] who describe water soluble, viscous compounds of low thermal stability. The aryloxides are crystalline solids, insoluble in water, possessing great thermal stability. The hexaphenoxy- (I; R = Ph) and octaphenoxy-derivatives (II; R = Ph) can be recovered unchanged after 26 hours' heating at 300°. All the esters, both alkyl and aryl, once formed are reasonably stable to water. However, great care must be taken to ensure complete dryness of solvents and reagents in these preparations, as otherwise little or none of the desired products is obtained. The presence of moisture probably accounts for many of the earlier failures in this field (cf. ref. 2). In the pyridine method, any moisture present produces almost immediately a deeply coloured solution, whose intensity increases, and the yields of desired products decreases, with increasing amounts of water. When reagents and solvents are rigorously dried, the reaction mixtures remain water-white. When hexaethoxycyclotriphosphazatriene was heated with n-butanol in refluxing benzene, no exchange reaction was observed, and the starting material was recovered.

The main phosphorus–nitrogen ring vibration in the infrared region of the spectrum was observed at higher frequency for the aryloxy- [(I; R = Ar) ν 1250—1280 cm.$^{-1}$, (II; R = Ar) ν 1330—1350 cm.$^{-1}$], than for the alkoxy-derivatives [(I; R = alkyl) ν 1225—1240 cm.$^{-1}$, (II; R = alkyl) ν 1320—1325 cm.$^{-1}$], in line with their greater electron-withdrawing effects. This is also reflected in their basicities in nitrobenzene [(I and II; R = Ar) $pK_a' < -6·0$ to −5·2, (I and II; R = alkyl) pK_a' −2·0 to 2·0].[20] A shift to higher frequencies on passing from the six-membered to the eight-membered phosphorus-nitrogen ring, noted earlier,[2] was also observed.

In contrast to earlier reports (cf. ref. 2), infrared spectra and molecular-weight measurements show that no change in the ring-size occurs on converting the chlorides, by the above methods, to alkoxy- and aryloxy-derivatives. Infrared spectra also provide additional evidence that the compounds described here had not undergone the alkoxyphosphazene–oxophosphazane rearrangement.[12]

Experimental

Materials.—Hexachlorocyclotriphosphazatriene and octachlorocyclotetraphosphazatetraene were prepared by the method of Schenck and Römer,[21] or obtained commercially. In either case, they were recrystallised from light petroleum (b. p. 60—80°) to the literature m. p.'s.[2] Benzene and light petroleum were dried with sodium wire. Methanol was dried by distillation from magnesium; other aliphatic alcohols were dried by azeotropic distillation, using a distillation column packed with Fenské helices. Pyridine was dried by refluxing over, and distillation from, phosphoric oxide. Phenols were recrystallised from suitable solvents, and dioxan was purified as described by Vogel.[22]

Infrared Spectra.—Infrared spectra were measured as liquid films or potassium bromide

[19] Feakins, Last, and Shaw, *Chem. and Ind.*, 1962, 510.
[20] Feakins, Last, Neemuchwala, and Shaw, *Chem. and Ind.*, 1963, 164; and unpublished results.
[21] Schenk and Römer, *Ber.*, 1924, **57**, 1343.
[22] Vogel, " Practical Organic Chemistry," Longmans, 3rd Edn., London, 1956, p. 177.

discs, as appropriate, with a Perkin-Elmer " Infracord " spectrophotometer fitted with sodium chloride optics.

Syntheses.—Five syntheses are described in detail; the remainder are summarised in the Table.

(*a*) *Hexamethoxycyclotriphosphazatriene.* A solution of the hexachloro-compound (20 g., 0·0575 mole) in benzene (180 ml.) was added dropwise to a cold stirred solution from sodium (10 g., 0·435 atom) in excess of methanol (150 ml.). The temperature was maintained at 0° during this addition and, on its completion, stirring was continued for 1 hr. during which time the temperature was allowed to reach that of the room. After 48 hr. the mixture was diluted with diethyl ether (300 ml.) and the sodium chloride was removed by filtration. The filtrate was extracted with dilute hydrochloric acid (2 × 200 ml.; 5%) and the extract neutralised ($NaHCO_3$). This solution was extracted with chloroform (2 × 100 ml.) and then dried (Na_2SO_4) and evaporated to leave crystalline material (7·2 g.). The ether layer was washed with dilute sodium hydrogen carbonate (100 ml.) and water (2 × 100 ml.) to give more of the same product (4 g.). The combined yield (52%) was recrystallised from diethyl ether–light petroleum (2 : 1) to give *hexamethoxycyclotriphosphazatriene*, m. p. 48° (Found: C, 22·4; H, 5·6; N, 13·0; P, 28·9; OMe, 58·0%; *M*, 323. $C_6H_{18}N_3O_6P_3$ requires C, 22·4; H, 5·6; N, 13·1; P, 29·0; OMe, 57·9%; *M* = 321).

This compound can also be purified by molecular distillation. If conventional distillation is attempted extensive decomposition takes place.

(*b*) *Hexaethoxycyclotriphosphazatriene.* The hexachloro-compound (20 g., 0·0575 mole) was dissolved in pyridine (82 ml.). To the cooled and stirred solution, ethanol (62 ml.) was added dropwise. The temperature was maintained at 0—5° during the addition and the reaction mixture was stored overnight. Diethyl ether (300 ml.) was added with stirring, and the pyridinium chloride was removed by filtration. The filtrate was washed with dilute solutions of hydrochloric acid, sodium hydrogen carbonate, and water. The solution was dried (Na_2SO_4) and the solvent removed. Two distillations gave *hexaethoxycyclotriphosphazatriene*, b. p. 115—116°/0·1 mm. (8·0 g., 23%) (Found: C, 35·5; H, 7·2; N, 10·6. $C_{12}H_{30}N_3O_6P_3$ requires C, 35·6; H, 7·4; N, 10·4%).

(c) *Hexaisopropoxycyclotriphosphazatriene.* Sodium (10·6 g., 0·48 g. atom) was dissolved in excess of dry isopropyl alcohol (180 ml.) and the hexachloro-compound (10 g., 0·029 mole) then added slowly to this solution. The mixture was heated under reflux for one week. Water (100 ml.) was added and the mixture was extracted with diethyl ether (2 × 300 ml.). The extract was washed with dilute hydrochloric acid, sodium hydrogen carbonate, and water. The solution was dried (Na_2SO_4) and the solvent mixture removed. Two distillations of the residue gave *hexaisopropoxycyclotriphosphazatriene*, b. p. 104—106°/0·005 mm. (4·4 g., 27·5%). This compound solidifies on storage and has m. p. ~28° (Found: C, 44·1; H, 8·4; N, 8·4. $C_{18}H_{42}N_3O_6P_3$ requires C, 44·2; H, 8·6; N, 8·6%).

(*d*) *Hexaphenoxy- and chloropentaphenoxy-cyclotriphosphazatriene.* Sodium (7·7 g., 0·335 g. atom) was dissolved in ethanol (100 ml.). Phenol (31·5 g., 0·335 mole) in ethanol (50 ml.) was added, and the mixture was boiled. The ethanol was slowly removed and replaced by anhydrous dioxan (170 ml.). Reflux conditions were maintained during the dropwise addition of the hexachloro-compound (15 g., 0·043 mole) in diethyl ether–dioxan (30 ml. : 70 ml.). The addition lasted 1 hr. and the mixture was boiled for a further 15 min. The cooled solution was diluted with light petroleum (b. p. 60—80°) (400 ml.) and was washed with water (120 ml.) It was then washed successively with dilute acid, sodium hydrogen carbonate, and water. The solution was dried (Na_2SO_4) and then evaporated to remove solvent. The residual yellow oil was dissolved in 50% (v/v) benzene–light petroleum and the solution passed through a short column packed with alumina. A part of the benzene eluate crystallised slowly and was recrystallised from benzene–light petroleum (b. p. 60—80°) (40 : 1) to give *hexaphenoxycyclotriphosphazatriene*, m. p. 110—111°, b. p. 280°/0·1 mm. (5·5 g., 18·5%) (Found: C, 62·4; H, 4·3; N, 6·2. $C_{36}H_{30}N_3O_6P_3$ requires C, 62·3; H, 4·3; N, 6·1). An oil, which separated from the above crystals, solidified later and was recrystallised as above to give *chloropentaphenoxycyclotriphosphazatriene*, m. p. 67—68° (4·2 g., 16%) (Found: C, 56·5; H, 3·9; Cl, 5·6; N, 6·5. $C_{30}H_{25}ClN_3O_5P_3$ requires C, 56·9; H, 3·9; Cl, 5·6; N, 6·7%).

(*e*) *Octa(2-naphthoxy)cyclotetraphosphazatetraene.* Sodium (7·4 g., 0·32 g. atom) was dissolved in ethanol (100 ml.), and to the solution was added 2-naphthol (46·5 g., 0·325 mole) in ethanol (180 ml.). The solution was boiled and the ethanol was removed and replaced by

Alkoxy- and aryloxy-cyclophosphazenes, $N_3P_3(OR)_6$ and $N_4P_4(OR)_8$.

No.	R	Ring size	Method	Yield (%)	B. p.	n_D^{25}	M. p.	Solvent for recrystn.
1	Pr^n	6	*b*	35·5	146—148°/ 0·1 mm.	1·4494	—	—
2	Bu^n	6	*b* (room temp.)	20·5	162—164°/ 0·01 mm.†	1·4330	—	—
3	$PhCH_2$	6	*e*	45	—	—	51·5°	C_6H_6–Pet * (10 : 1)
4	*p*-MeO·C_6H_4	6	*e*	90	—	—	103—104	EtOH
5	2-$C_{10}H_7$ (2-naphthyl)	6	*e*	46·5	—	—	168—169	$CHCl_3$
6	Me	8	*b* (−10°)	48·5	125°/ 0·1 mm	—	41	C_6H_6–Pet (1 : 50)
			a (room temp.)	84	—	—	41	C_6H_6–Pet (1 : 50)
7	Et	8	*b*	72	128°/ 0·001 mm.	—	45—47 ‡	Pet
8	Pr^n	8	*b*	83	176—178°/ 0·01 mm.	—	38—38·5 ‡	—
9	Pr^i	8	*c*	58·5	~130°/ 0·01 mm. (decomp.)	—	74—75 (decomp.) ‡	—
10	Bu^n	8	*b*	66	196—198°/ 0·005 mm.	1·4565	—	—
11	$PhCH_2$	8	*e*	27	—	—	38—39	C_6H_6–Pet (50 : 1)
12	Ph	8	*e*	87	—	—	85—86	C_6H_6–Pet (50 : 1)
13	*p*-MeO·C_6H_4	8	*e*	70	—	—	73—74	C_6H_6–Pet (1 : 1)

	Found					Required			
No.	C (%)	H (%)	N (%)	*M*	Formula	C (%)	H (%)	N (%)	*M*
1	44·8	8·5	8·7	—	$C_{18}H_{42}N_3O_6P_3$	44·2	8·6	8·6	—
2	49·8	9·2	6·8	—	$C_{24}H_{54}N_3O_6P_3$	50·3	9·4	7·3	—
3	64·7	5·5	5·6	787	$C_{42}H_{42}N_3O_6P_3$	64·8	5·4	5·4	777
4	54·8	4·8	4·8	—	$C_{42}H_{42}N_3O_{12}P_3$	57·7	4·8	4·8	—§
5	71·2	3·9	4·2	—	$C_{80}H_{42}N_3O_6P_3$	72·5	4·2	4·2	—
6	22·7	5·7	13·1	415	$C_8H_{24}N_4O_8P_4$	22·5	5·6	13·1	428 ¶
7	35·4	7·1	10·4	—	$C_{16}H_{40}N_4O_8P_4$	35·6	7·4	10·4	—
8	44·4	8·5	8·7	—	$C_{24}H_{56}N_4O_8P_4$	44·2	8·6	8·6	—
9	44·3	8·6	8·6	—	$C_{24}H_{56}N_4O_8P_4$	44·2	8·6	8·6	—
10	50·8	9·6	7·9	—	$C_{32}H_{72}N_4O_8P_4$	50·3	9·4	7·3	—
11	64·0	5·6	5·4	959	$C_{56}H_{56}N_4O_8P_4$	64·9	5·4	5·4	1032
12	62·0	4·3	6·0	926	$C_{48}H_{40}N_4O_8P_4$	62·3	4·3	6·0	924
13	57·8	4·8	4·7	—	$C_{56}H_{56}N_4O_{16}P_4$	57·7	4·8	4·8	—

* Pet = light petroleum (b. p. 60—80°). † Lit.,[3] b. p. 170—171°/0·03 mm. ‡ Purified by vacuum sublimation. § Found: P, 10·2. Requires P, 10·6%. ¶ Found: P, 28·4. Requires P, 29·0.

dioxan (200 ml.). The octachloro-compound (15 g., 0·0325 mole) in benzene (100 ml.) was added dropwise and the mixture was boiled for 3 hr. The cooled mixture was diluted with diethyl ether (300 ml.) and was washed successively with dilute hydrochloric acid, sodium hydrogen carbonate, and water. The solution was dried (Na_2SO_4) and the solvent mixture removed. The crude product solidified and had m. p. ~110° (41·9 g., 98%). Three recrystallisations from acetone gave *octa*(2-*naphthoxy*)*cyclotetraphosphazatetraene*, m. p. 126—127° (Found: C, 72·2; H, 4·2; N, 4·2. $C_{80}H_{56}N_4O_8P_4$ requires C, 72·5; H, 4·2; N, 4·2%).

The Hydrolytic Degradation of Hexamethoxycyclotriphosphazatriene.—The ester (I; R = Me) (1·2502 g.) together with 10% aqueous hydrochloric acid (25 ml.) was sealed into a thick-walled tube (12 mm. int. dia.). The initially heterogeneous mixture was heated for 45 hr. at 160°. The now homogeneous solution was transferred to a 50 ml. round-bottomed flask and the water removed under reduced pressure. Solid potassium hydroxide was added to the white pasty residue, and this was heated with a luminous Bunsen flame. A stream of nitrogen gas swept the volatile materials through a drying tube (KOH pellets) into a solution of ether saturated with hydrogen chloride. The resulting white precipitate was identified as ammonium chloride [0·4464 g. (73%)].

The same degradation procedure was applied, with similar results, to the other esters.

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