18. *Phosphorus–Nitrogen Compounds. Part V.*[1] *Friedel–Crafts Arylation of Hexachlorocyclotriphosphazatriene.*

By K. G. Acock, R. A. Shaw, and F. B. G. Wells.

Arylation of hexachlorocyclotriphosphazatriene by a number of hydrocarbons in the presence of aluminium chloride has been investigated. A number of crystalline phenyl-, tolyl-, and chlorophenyl-phosphazenes have been isolated and their structures determined by hydrolytic degradation. The mechanism of the arylation is discussed.

In Part I [2] of this series it was shown that the successive replacement of chlorine atoms in hexachlorocyclotriphosphazatriene by dimethylamine residues followed, for the compounds then isolated, a non-geminal [2,3] reaction pattern. Evidence is now presented for the alternative, geminal scheme in the Friedel–Crafts arylation of hexachlorocyclotriphosphazatriene with anhydrous aluminium chloride as catalyst. A preliminary account of part of this work has appeared.[4] Bode and Bach [5] had previously reported the synthesis of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene, $N_3P_3Ph_2Cl_4$ (I), by the above method and had tried unsuccessfully to prepare higher phenylation products. We have re-investigated this phenylation in some detail:

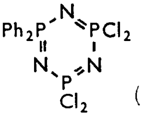
$$N_3P_3Cl_6 + PhH\ (excess) \xrightarrow{AlCl_3} N_3P_3Ph_nCl_{6-n} + nHCl$$

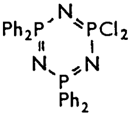
Throughout this work the molar ratio of chlorophosphazene to aluminium chloride was 1 : 2. Greater proportions of the catalyst (*e.g.*, 1 : 6), added either all at once [5] or in portions over a period of days, failed to increase noticeably the yield for a given reaction time. To obtain adequate yields (25—40%) of the diphenyl compound (I) ($n = 2$), it is necessary to run the reaction for several days at the reflux temperature of the benzene solution. 2,2-Dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene, $N_3P_3Ph_4Cl_2$ (II) ($n = 4$), was

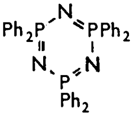
---

[1] Part IV, Ray, Shaw, and Smith, *J.*, 1963, 3236.
[2] Ray and Shaw, *J.*, 1961, 872.
[3] Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.
[4] Shaw and Wells, *Chem. and Ind.*, 1960, 1189.
[5] Bode and Bach, *Ber.*, 1942, **75**. 215.

isolated in 16% yield, together with a 41% yield of the diphenyl derivative (I), by careful fractional crystallisation, or by chromatography, of the oily product obtained after the reaction period had been extended to six weeks. No appreciable amount of this compound was formed in the normal conditions employed for the preparation of the diphenyl derivative (I) but, already in this case, the relatively long periods of refluxing (usually 2—7 days) indicated the sluggish nature of the reaction. An improved yield (46%) of the tetraphenyl derivative (II), with a small amount (5%) of the hexaphenyl compound (III), was obtained when the diphenyl compound (I) was used as starting material in the six-weeks reaction. When the Friedel–Crafts reaction was carried out for 48 hours at 150° in a stainless-steel autoclave, a 20% yield of the hexaphenyl derivative, $N_3P_3Ph_6$ (III) ($n = 6$), was isolated. Yields are generally very low when this compound is obtained by Grignard reactions [5,6] or by cyclisation.[7] If, in the above high-temperature reaction, the aluminium chloride is omitted, hexachlorocyclotriphosphazatriene is recovered quantitatively, showing the catalyst to be essential. No other phenylchlorophosphazene was isolated, although sought.


(I)


(II)

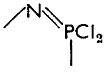

(III)

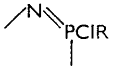
The geminal structure of the diphenyl compound (I) had been shown by Bode and Bach [5] and was confirmed by us. The geminal nature of the tetraphenyl derivative (II) was proved by a similar hydrolytic degradation involving isolation of diphenylphosphinic acid, $Ph_2PO{\cdot}OH$, as well as by estimation of phosphoric acid in the aqueous layer:

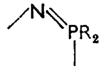
$$N_3P_3Ph_2Cl_4 \longrightarrow Ph_2PO{\cdot}OH + 2H_3PO_4$$
$$N_3P_3Ph_4Cl_2 \longrightarrow 2Ph_2PO{\cdot}OH + H_3PO_4$$

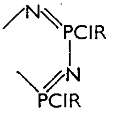
The above results raise questions about the cause of the very slow rate of the reaction, whether the same replacement pattern of chlorine atoms holds for other aryl residues, and in general, about the scope and limitations of Friedel–Crafts arylations applied to hexachlorocyclotriphosphazatriene.

We consider the basic ring units (A—D) in the arylation:


(A)


(B)


(C)


(D)

it appears that when R = Ph the chlorine atom of structure (B) departs more readily with the electron pair of its bond with phosphorus than is the case with the corresponding chlorine atom in (A), thus giving rise to the geminal grouping (C); *i.e.*, in this system a phenyl group facilitates the heterolysis to a chloride ion more than another chlorine atom does, and has thus so far prevented the isolation of the monophenyl derivative, $N_3P_3PhCl_5$, as well as of other non-geminal structures (D) which, if present at all, are only minor constituents of the reaction mixtures. This is not unexpected in the light of the general theory of reaction mechanism, and the mechanism of the electrophilic Friedel–Crafts reaction in particular. If by suitable choice of the groups R the electron supply to the reacting phosphorus–chlorine bond is increased relative to that to the phenyl group, the

[6] Rosset, *Compt. rend.*, 1925, **180**, 750.

[7] Haber, Herring, and Lawton, *J. Amer. Chem. Soc.*, 1958, **80**, 2116; Korshak, Gribova, Artamonova, and Bushmarina, *Vysokomol. Soedineniya*, 1960, **2**, 377.

same geminal products (C) should result; conversely, if the electron supply is reduced, structure (B) might be isolable, which in turn could yield then either (C), or with even greater deactivation of the bond in question the non-geminal structure (D). All this assumes, of course, that steric effects remain reasonably constant.

Supporting evidence for this hypothesis comes from recent observations.[8] 2,2,4,6-Tetrachloro-4,6-bisdimethylaminocyclotriphosphazatriene, $N_3P_3Cl_4(NMe_2)_2$ (D; R = NMe_2), is converted by a Friedel–Crafts reaction into 2,2-dichloro-4,6-bisdimethylamino-4,6-diphenylcyclotriphosphazatriene, $N_3P_3Ph_2Cl_2(NMe_2)_2$. Relative to the ring unit (A), structure (B; R = NMe_2) will have an increased electron supply to phosphorus, thus directing a second dimethylamino-group to another phosphorus atom,[2] *viz.*, (D; R = NMe_2), but favouring electrophilic attack on chlorine on structure (B) [a fact borne out by the much greater ease of diphenylation of this compound than of the hexachloro-derivative (I) [8b]], giving a grouping (C) (one R = NMe_2, the other R = Ph).[8] Thus, although the two phenyl groups are non-geminal with respect to each other, the replacement of chlorine atoms in this Friedel–Crafts phenylation still follows a geminal pattern. In addition to polar effects, the above electrophilic reaction should also be less susceptible to steric hindrance than further nucleophilic attack by dimethylamine on the same phosphorus atom.

Attempts to extend the Friedel–Crafts reaction to aromatic compounds with an electron supply greater than the phenyl group met only with limited success. The sluggish nature of the reaction necessitated forcing conditions which led to considerable, sometimes overwhelming, side-reactions between the catalyst and the more reactive aromatic compounds.[9] In addition, problems of isomerism, due to the relative positions (on initial reaction and/or subsequent migration [10]) of the substituents in the aryl residue, were encountered.

A mixture of isomeric 2,2-diphenyl-4,4,6,6-tetratolylcyclotriphosphazatrienes, $N_3P_3Ph_2(C_6H_4Me)_4$ (IV), was prepared from the diphenyl derivative (I) and toluene. Even in compounds carrying only one geminal pair of tolyl residues there are six theoretically possible orientations of the methyl groups with respect to the phosphorus atoms. Thus, although the mixture gave satisfactory analyses, the crystalline product melted over a range.

The isomeric 2,2,4,4-tetrachloro-6,6-ditolylcyclotriphosphazatrienes, $N_3P_3(C_6H_4Me)_2Cl_4$ (VA), were prepared by an 80-hour reaction in boiling toluene. Crystalline material with a melting point range (110—117°) was obtained and a geminal reaction pattern is suggested from the results of hydrolysis, *i.e.*, the isomerism is due to the orientation of the aromatic methyl group with respect to the phosphorus atom. From this mixture, one isomer, 2,2,4,4-tetrachloro-6,6-di-*p*-tolylcyclotriphosphazatriene (VB), m. p. 124—126°, was isolated in a pure state, the *p*-orientation being in line with findings for phosphinolation.[11,12] A crystalline mixture of isomeric dichlorotetratolylcyclotriphosphazatrienes (VI) was also prepared.

Some evidence for the formation of di- and tetra-xylyl derivatives was obtained, but reactions with mesitylene, 1,2,4,5-tetramethylbenzene, anisole, biphenyl, thiophen, and furan were unsuccessful. Muetterties,[13] in a study of the reaction between boron trichloride and aromatic hydrocarbons in the presence of aluminium chloride, obtained analogous results which illuminate our findings. For example, a 15% yield of dichloro-2,5-xylylborane was reported from experiments at 140° with mesitylene.

[8] (*a*) Bezman and Ford, *Chem. and Ind.*, 1963, 163; (*b*) Shaw and Stratton, unpublished results.

[9] Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, 1941.

[10] Olah, Tolgyesi, and Dear, *J. Org. Chem.*, 1962, **27**, 3441, 3449, 3455; Olah and Meyer, *ibid.*, p. 3464.

[11] Kosolapoff, *J. Amer. Chem. Soc.*, 1952, **74**, 4119.

[12] Schmutzler, *Chem. and Ind.*, 1962, 1868; and personal communication.

[13] Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 2597; 1960, **82**, 4163.

The scope of the Friedel–Crafts reaction is widened by inclusion of aromatic hydrocarbons carrying electron-withdrawing groups. The reaction with chlorobenzene was studied:

$$N_3P_3Cl_6 + \text{PhCl (excess)} \xrightarrow{AlCl_3} N_3P_3(C_6H_4Cl)_nCl_{6-n} + n\text{HCl}$$

Its decreased reactivity towards this type of reaction is more than balanced by the higher reaction temperature achieved at its boiling point. There is also less tar formation than in reactions with alkylbenzenes. In reactions allowed to run for 42 hours, pentachloro-*p*-chlorophenylcyclotriphosphazatriene, $N_3P_3(C_6H_4Cl\text{-}p)Cl_5$ (VII) ($n = 1$) and two isomeric derivatives, 2,2,4,4-tetrachloro-6,6-di-*p*-chlorophenylcyclotriphosphazatriene, $N_3P_3(C_6H_4Cl\text{-}p)_2Cl_4$, m. p. 138—139° (VIII) ($n = 2$), and 2,2,4,4-tetrachloro-6,6-bischlorophenylcyclotriphosphazatriene, $N_3P_3(C_6H_4Cl)_2Cl_4$, m. p. 118—120° (IX) ($n = 2$), were formed, the monochlorophenyl derivative (VII) being the first example in this series of non-pairwise replacement of chlorine atoms achieved by means of the Friedel–Crafts reaction. With longer reaction times (up to 11 days) a tetrakis-compound, 2,2-dichloro-4,4,6,6-tetra-*p*-chlorophenylcyclotriphosphazatriene, $N_3P_3(C_6H_4Cl\text{-}p)_4Cl_2$ (X) ($n = 4$), and a fully arylated derivative, hexa-(*p*-chlorophenyl)cyclotriphosphazatriene, $N_3P_3(C_6H_4Cl\text{-}p)_6$ (XI) ($n = 6$), were isolated.

The structures of the chlorophenylphosphazenes, like those of the tolyl derivatives, present two problems of isomerism: (*a*) the positions of the aryl residues on the phosphazene ring, and (*b*) the substitution pattern of the aromatic ring. The former was solved in all cases by hydrolytic degradation, isolation of the corresponding phosphonic and phosphinic acids, and estimation of phosphate ion (cf. Table). In all the compounds characterised in these arylations the geminal replacement of chlorine atoms is followed (mono-, like penta- and hexa-derivatives, being structures common to both geminal and non-geminal patterns). As electron-withdrawing substituents, such as chlorine, in the aryl group have permitted the isolation of the structural unit (B), further work along similar lines might lead to non-geminal structures such as (D).

Hydrolytic degradation of arylphosphazenes.

Compound	2,2,4,4,6,6-Subst.	Period of heating (days)	Temp.	Phosphonic or phosphinic acid		Phosphate (mol.)
				identity	(mol.)	
(I)	Cl_4Ph_2	2·3	165°	$Ph_2PO{\cdot}OH$ *	0·99	2·0
(II)	Cl_2Ph_4	3·0	165	,,	1·95	0·99
(VB)	$Cl_4(C_6H_4Me\text{-}p)_2$	3·0	150	$(C_6H_4Me\text{-}p)_2PO{\cdot}OH$ †	0·90	1·90
(VA) ‡	$Cl_4(C_6H_4Me)_2$	2·7	155	—	—	1·94
(VII)	$Cl_5(C_6H_4Cl\text{-}p)$	4·0	170	$C_6H_4Cl\text{-}p{\cdot}PO(OH)_2$ §	0·97	1·85
(VIII)	$Cl_4(C_6H_4Cl\text{-}p)_2$	4·0	170	$(C_6H_4Cl\text{-}p)_2PO{\cdot}OH$ ¶	0·84	1·80
(IX)	$Cl_4(C_6H_4Cl)_2$	4·0	170	$(C_6H_4Cl)_2PO{\cdot}OH$ **	0·93	1·98
(X)	$Cl_2(C_6H_4Cl\text{-}p)_4$	4·0	170	$(C_6H_4Cl\text{-}p)_2PO{\cdot}OH$ ¶	1·94	0·90
(XI)	$(C_6H_4Cl\text{-}p)_6$	7·0	250	,,	2·76	—

* M. p. and mixed m. p. 192—193°. † M. p. 128—130° (lit.,[15] 130—132°). ‡ Isomers, m. p. 110—117°; corresponding ditolylphosphinic acids not separated. § M. p. and mixed m. p. 187—188°. ¶ M. p. and mixed m. p. 139°. ** M. p. 171—173°, see text.

The latter problem (*b*), amounting to the separation and identification of the respective phosphonic and phosphinic acids obtained from the degradations, resembles that encountered in the phosphinolation of aromatic compounds, although in the latter case the phosphorus compound is tervalent. Despite the fact that Friedel–Crafts reactions with phosphorus trichloride are simpler than the examples under discussion (higher reactivity, one phosphorus atom only, etc.), relatively little information is available about orientation in this system. Kosolapoff[11] studied the orientation of the methyl group in the reaction with toluene and reported a 6·3 : 2·7 : 1·0 ratio for *para*- : *meta*- : *ortho*-isomers. Schmutzler[12] re-investigated this system and found a *para-* : *meta*-isomer ratio of 2—3 : 1, no *ortho*-derivative being observed. He also reported [12] two isomers in the reaction with chlorobenzene and a number of other substituted benzenes, and assigned *para-* and *meta*-structures by analogy. Other workers [14] reported similarly *para-* and *meta*-isomers for ethylbenzene, but *para-* and *ortho*-isomers for chlorobenzene.

As mentioned earlier, the only pure compound obtained from the phosphazenylation of toluene was the 6,6-di-*p*-tolyl derivative. It can be seen from the Table that in the chlorobenzene system four of the five pure compounds isolated had been substituted in the *para*-positions of all the chlorobenzene molecules involved. The fifth compound gave on hydrolytic degradation a new acid, bischlorophenylphosphinic acid. For this the *p,p'*-, *m,m'*-, and *p,m'*-structures could be ruled out by comparison with the authentic acids. Examination of its infrared spectrum suggests a *p,o'*-structure.

It must be emphasised that the chlorobenzene reaction is very complex (cf. ref. 10) and that the chlorophenylphosphazenes isolated may represent only some of the products. Nevertheless, it seems likely that the preferred reaction site is *para* to the chlorine atom, with the reservation that some of the products isolated could have arisen from reactions [10] subsequent to the original phosphazenylation. It seems thus, from the evidence at present available, that phosphazenylation of substituted benzenes follows broadly the same pattern as phosphinolation (little information being available on Friedel–Crafts reactions with quinquevalent phosphorus compounds [9,15]), with perhaps an even greater preference for the *para*-position.

Great difficulties were experienced with reactions involving bromobenzene or 1,2-dichlorobenzene. The very complex behaviour of these compounds with aluminium halides has recently been investigated by Olah and his co-workers.[10] No chlorophosphazene was recovered and the only crystalline products isolated were 4-bromobiphenyl and a bisbromophenylphosphazene, $N_3P_3(C_6H_4Br)_2Cl_4$. The presence of the former is of interest as Olah and his co-workers [10] reported small quantities of chlorobiphenyl in the reaction system chlorobenzene–aluminium chloride, but could not detect any bromobiphenyl in the corresponding study with bromobenzene. It is possible that the presence of a third component in our system may have favoured the biaryl formation. Increased biaryl formation due to an additional component in a free-radical reaction has recently been reported by Hey, Perkins, and Williams.[16]

The main feature of Bode and Bach's [5] proposal, favoured also by later workers,[17] regarding the mechanism of Friedel–Crafts arylation of hexachlorocyclotriphosphazatriene is based on the ratio of the reactants and the isolation of a material of composition $N_3P_3Cl_6,2AlCl_3$. For this a doubly ionised structure (with suitable resonance forms) $[N_3P_3Cl_4]^{2+}2[AlCl_4^-]$ has been put forward.[5,17] It is notoriously difficult to deduce the nature of the catalytically active species from the bulk properties of solid or solution complexes. For the solid complex a doubly positively charged structure seems, however, inherently unlikely, and probably the donor properties of the ring-nitrogen atoms [18,19] play an important part. Lindqvist [20] has independently come to a similar conclusion.

The species responsible for the reaction probably involves a quasi-phosphonium ion, *e.g.*, $N_3P_3Cl_5^+$, or a related structure, which reacts with the aromatic hydrocarbon or in other ways. It is worth mentioning that it was never possible to obtain a material balance to account for all the hexachlorocyclotriphosphazatriene used. Some phosphorus-containing species was always found in the aqueous phase, after the hydrolytic working-up.

[14] Baldwin, Smitheman, and Washburn, *J. Org. Chem.*, 1961, **26**, 3547.

[15] Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, 1950.

[16] Hey, Perkins, and Williams, *Chem. and Ind.*, 1963, 83.

[17] Becke-Goehring and John, *Z. anorg. Chem.*, 1960, **304**, 126.

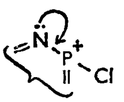
[18] Feakins, Last, and Shaw, *Chem. and Ind.*, 1962, 510; Feakins, Last, Neemuchwala, and Shaw, *ibid.*, 1963. 164; and unpublished results.

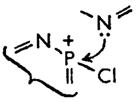
[19] Das, Shaw, and Smith, and (in part) Last and Wells, *Chem. and Ind.*, 1963, 866; and unpublished results.

[20] Lindqvist, personal communication.

A quasi-phosphonium ion has also been postulated in the catalytic polymerisation of the hexachloro-compound.[3,21] The assignment of the stereochemical configurations [8a] of the starting materials from the structures of the resultant Friedel–Crafts arylation products [8a] may run, if quasi-phosphonium ions are involved, into the same difficulties of interpretation as were encountered with carbonium ions. The slow rate of the phosphazenylation

(E)

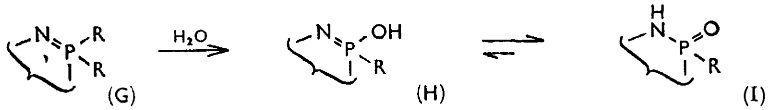




(F)

is probably due to the bulk of the reactive species and the dissipation of the positive charge at the reaction site by an intramolecular (E) or intermolecular co-ordination (F) with a ring-nitrogen atom. The basicity of hexachlorocyclotriphosphazatriene in nitrobenzene solution towards perchloric acid increases markedly with increasing replacement of chlorine atoms by phenyl groups.[18] It seems feasible that this is paralleled by a similar increase in ring-nitrogen donor properties towards aluminium chloride. This, as well as a greater tendency to the above mentioned co-ordination to the quasi-phosphonium ion, will probably contribute to the increasing difficulty of progressive replacement of chlorine atoms by phenyl residues by this mechanism.

Qualitative experiments established that the ease of hydrolysis in solution decreases rapidly in the order $N_3P_3Cl_6 > N_3P_3Ph_2Cl_4 > N_3P_3Ph_4Cl_2$. Thus, treating hexachlorocyclotriphosphazatriene in dioxan with aqueous potassium acetate at 50° for 5 hr. converts it in high yield into the tripotassium salt of the hydroxyoxophosphazane $[N_3H_3P_3O_6]K_3$.[22] In similar conditions, even with an extended reaction time (23 hr.), 30% of the diphenyl compound (I) and quantitative yields of the tetraphenyl derivative (II) were recovered. The lower reactivity towards hydrolysis of the phosphazene chlorine atoms with their increased replacement by other groups follows a similar trend as in aminolysis,[1,2,23] alcoholysis,[24] and mercaptolysis.[25] Hydrolysis, however, differs from these other reactions, in so far as the resultant partial or complete hydrolysis products almost certainly undergo a phosphazene–phosphazane prototropic shift [3] with the resultant partial or complete loss of phosphazene character of the ring [cf. (G) $\longrightarrow$ (H) $\longrightarrow$ (I)].



On present evidence it seems that the ease of hydrolysis of the phosphazanes differs considerably from that of the phosphazenes,[3] and hence care should be taken when discussing the hydrolytic stability of the phosphazene ring to differentiate between hydrolytic attack involving the substitutents and attack directly on the ring. When account of this is taken, it will probably be found that the hydrolytic stability of the phosphazene ring is considerably greater than is often assumed.

EXPERIMENTAL

Microanalyses were carried out by the Microanalytical Laboratory, Imperial College of Science and Technology, London. Phosphate was determined gravimetrically by double precipitation as magnesium ammonium phosphate $MgNH_4PO_4,6H_2O$, followed by ignition to the

---

[21] Konecny and Douglas, *J. Polymer Sci.*, 1959, **36**, 195; Konecny, Douglas, and Gray, *ibid.*, 1960, **42**, 383; Shaw, *ibid.*, 1961, **50**, 21.

[22] Nielsen and Morrow, *Inorg. Synth.*, 1960, **6**, 97; Fitzsimmons, Hewlett, and Shaw, unpublished results.

[23] Hills and Shaw, following paper; Capon, Hills, and Shaw, *Proc. Chem. Soc.*, 1962, 390; and unpublished results.

[24] Dell, Fitzsimmons, and Shaw, unpublished results.

[25] Carroll and Shaw, *Chem. and Ind.*, 1962, 1908; and unpublished results.

pyrophosphate. M. p.s were determined by means of an oil-bath or, where specifically indicated, of a Reichert–Kofler micro-heating stage fitted to a polarising microscope.

Light petroleum (unless otherwise stated) of b. p. 60—80°, benzene, and toluene were distilled from sodium wire. Chlorobenzene was dried over calcium sulphate. Silica gel (M.F.C. grade from Messrs. Hopkin & Williams) was heated to the temperature and for the time stated. The composition of the chromatographic eluant is indicated after the product obtained.

Hexachlorocyclotriphosphazatriene was recrystallised from light petroleum before use. Freshly purchased aluminium chloride, instantly fuming on exposure to air, was used.

2,2,4,4-*Tetrachloro*-6,6-*diphenylcyclotriphosphazatriene* (I).—Prepared by the method of Bode and Bach [5] but with the concentration of unused chlorophosphazene in the reaction crude reduced by vacuum-sublimation (50—55°/0·8 mm. for 24 hr.); yields do not exceed 19—20%. Pure material recrystallised from chloroform–light petroleum (1 : 9) had m. p. 95·5° (lit.,[5] 92·5°) (Found: C, 33·95; H, 2·95; N, 9·85; P, 21·1. Calc. for $C_{12}H_{10}Cl_4N_3P_3$: C, 33·4; H, 2·3; N, 9·75; P, 21·6%). Better yields (35—40%) are obtained if starting material is separated by column chromatography. In a typical example, hexachlorocyclotriphosphazatriene (7·5 g., 0·0216 mole) was dissolved in dry benzene (65 ml.), and powdered anhydrous aluminium chloride (5·8 g., 0·0434 mole) quickly added. The flask was fitted with a condenser carrying a P_2O_5 guard-tube and boiling with reflux was maintained for 72 hr. by immersion in an oil-bath (95—100°). The cooled reaction mixture was then poured into ice and 2N-hydrochloric acid (200 ml.). The aqueous layer, after extraction with benzene (2 × 75 ml.), was rejected and the combined benzene fractions were washed with distilled water before drying (Na_2SO_4). The pale yellow crude product obtained by evaporation of the solvent at room temperature (rotary film evaporator) was then passed in light petroleum (b. p. 80—100°) down a silica gel column (40 × 2 cm.) prepared from gel heated to 110° for 18 hr. Unchanged chlorophosphazene was removed from the column by elution with light petroleum (1—1·5 l.). The required product (I) (35%) was eluted with light petroleum–benzene (4 : 1).

In an experiment with a 6 : 1 molar ratio of aluminium chloride to the hexachloro-compound, a third of the catalyst at a time was added to the reaction mixture at the start, and after 2 and 4 days. After 7 days the reaction was stopped. Some aluminium chloride remained undissolved. The mixture was worked up as described above and the diphenyl compound (I) was obtained in 43% yield by fractional crystallisation from light petroleum. No tetraphenyl compound (II) was observed.

When the hexachloro-compound (1·1 g.) had been heated in a heavy-walled glass tube with dry benzene (10 ml.) at 150° for 48 hr. it was recovered quantitatively. Reactions were attempted in boiling 1 : 2 benzene–carbon disulphide in the presence of aluminium chloride, but no phenylated product was identified.

2,2-*Dichloro*-4,4,6,6-*tetraphenylcyclotriphosphazatriene* (II).—(*a*) *From hexachlorocyclotriphosphazatriene.* The reaction, with identical quantities, was carried out as described for the diphenyl derivative (I), but boiling under reflux was continued for 6 weeks. The tetraphenyl compound (II) was obtained in 16% yield, together with a 41% yield of (I), by careful fractional crystallisation from light petroleum (b. p. 80—100°; 200 ml.). Crystallisation occurred after several days in the refrigerator and crops of alternate crystalline materials were obtained by first one-fold and then four-fold reductions in volume. 2,2-*Dichloro*-4,4,6,6-*tetraphenylcyclotriphosphazatriene,* m. p. 142—143° (Found: C, 56·1; H, 3·6; N, 8·1; Cl, 14·2; P, 17·9%; *M*, 499. $C_{24}H_{20}Cl_2N_3P_3$ requires C, 56·05; H, 3·9; N, 8·2; Cl, 13·8; P, 18·05%; *M*, 514), was obtained by recrystallising the combined fractions of m. p. 133—140° from chloroform–light petroleum (1 : 9).

(*b*) *From* 2,2,4,4-*tetrachloro*-6,6-*diphenylcyclotriphosphazatriene* (I). An improved preparation of the tetraphenyl compound (II) was developed by Dr. K. Hills. The diphenyl compound (I) (6·43 g., 0·0149 mole) was heated with an excess of boiling benzene (60 ml.) for 6 weeks in the presence of anhydrous aluminium chloride (3·98 g., 0·0298 mole). The mixture was poured into 2N-hydrochloric acid (150 ml.), and the aqueous layer washed with benzene (2 × 30 ml.). The organic layer was washed with sodium hydrogen carbonate solution and water, then dried (Na_2SO_4), and the benzene was removed. The residual oil was dissolved in hot light petroleum (300 ml.). Careful crystallisation gave starting material (I) (0·42 g., 6·5%) and 4·22 g. of solid, m. p. 120—137°. The latter was recrystallised from ether; hexaphenylcyclotriphosphazatriene (0·45 g., 5%) separated first (m. p. and mixed m. p. 231—233°), followed by the tetraphenyl derivative (II) (3·51 g., 46%; m. p. and mixed m. p. 142°). As an alternative, the chromatographic procedure described above can be used to obtain pure di- and tetraphenyl compounds, the latter being eluted by benzene–ether (20 : 1).

Hexaphenylcyclotriphosphazatriene (III).—A solution of hexachlorocyclotriphosphazatriene (11·6 g., 0·033 mole) in benzene (100 ml.) was poured into the stainless-steel reaction chamber of a Baskerville and Lindsay autoclave which, after addition of pulverised anhydrous aluminium chloride (8·8 g., 0·066 mole), was quickly sealed. After heating (48 hr.) at 150° ± 5° (5—8 atm.), with stirring, the products were poured into ice and 2N-hydrochloric acid. Hexaphenylcyclotriphosphazatriene, m. p. and mixed m. p. 232—233° (3·6 g., 20%) (Found: C, 72·5; H, 4·9; N, 6·7%; *M*, 597. Calc. for $C_{36}H_{30}N_3P_3$: C, 72·3; H, 5·1; N, 7·0%; *M*, 572), was obtained by crystallising the concentrate obtained from combined benzene fractions (as in previous experiments), together with that obtained by Soxhlet extraction (benzene) of "insoluble" material from the original reaction mixture, in 1 : 1 benzene–chloroform.

The absence of products (I) and (II) was established by concentrating the combined mother-liquors and extracting the residue with boiling light petroleum (300 ml.). The hexaphenyl derivative was also obtained from the diphenyl derivative (cf. above).

2,2-*Diphenyl*-4,4,6,6-*tetratolylcyclotriphosphazatrienes* (*Isomers*) (IV).—2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene (6·4 g., 0·0148 mole) was dissolved in toluene (65 ml.) and boiled under reflux (oil-bath, 125°), with a P_2O_5 guard tube, for 7 days in the presence of anhydrous aluminium chloride (4·0 g., 0·03 mole). The mixture was worked-up as described for the diphenyl derivative (I), but the pale oil obtained on hydrolysis and removal of the benzene–toluene mixture was only partially soluble in boiling light petroleum (100 ml.). The colourless crystalline residue (3 g.) melted in the range 190—215°. Successive recrystallisations from benzene–light petroleum (1 : 1) and chloroform–light petroleum (1 : 1) gave material, m. p. 228—240° (Reichert–Kofler), consisting of the isomeric 2,2-diphenyl-4,4,6,6-tetratolylcyclotriphosphazatrienes (IV) (Found: C, 73·0; H, 6·1; N, 6·5. Calc. for $C_{40}H_{38}N_3P_3$: C, 73·5; H, 5·9; N, 6·4%).

Tolylphosphazenes (V).—Hexachlorocyclotriphosphazatriene (20 g., 0·0575 mole) and pulverised anhydrous aluminium chloride (15 g., 0·115 mole) were dissolved in toluene (200 ml.) and boiled under reflux for 80 hr. in an oil-bath (125°). After removal of toluene *in vacuo* the reaction flask was placed in an ice-bath and fitted with a mechanical stirrer and dropping funnel. To avoid possible cleavage of activated carbon–phosphorus bonds [26] the residue was dissolved in anhydrous tetrahydrofuran and the aluminium chloride was hydrolysed by slow addition, with stirring, of a solution of a controlled amount of water (15 ml.) in tetrahydrofuran (100 ml.). The filtered solution (together with benzene washings) was dried ($MgSO_4$) and all solvents were removed under reduced pressure. The residual brown oil (34·4 g.) was extracted with boiling light petroleum (2 × 150 ml.), leaving a solid residue (10·8 g.). A portion of the petroleum extract (containing *ca.* 6 g.) was diluted to 150 ml. with the same solvent and chromatographed on a silica gel column (45 × 3 cm.; heated at 110° for 16 hr.). Elution yielded starting material (0·6 g., 10%) (light petroleum), a yellow oil (2·2 g.) (light petroleum–benzene, 1 : 1) which crystallised very slowly and after three recrystallisations from light petroleum–chloroform (4 : 1) gave a mixture of isomeric 2,2,4,4-tetrachloro-6,6-ditolylcyclotriphosphazatrienes (VA), m. p. 110—117° (2·0 g., 28%) (Found: C, 36·4; H, 3·1; Cl, 30·6; N, 9·1; P, 20·3. Calc. for $C_{14}H_{14}Cl_4N_3P_3$: C, 36·6; H, 3·1; Cl, 30·9; N, 9·2; P, 20·2%). Numerous further recrystallisations of this yielded 2,2,4,4-*tetrachloro*-6,6-*di*-p-*tolylcyclotriphosphazatriene* (VB), m. p. 124—126° (0·5 g., 7%) (Found: C, 37·1; H, 3·2; N, 8·2; P, 20·0; Cl, 30·6%). Further elution yielded an oil (1·2 g.) (light petroleum–benzene, 3 : 7) which on recrystallisation from light petroleum–chloroform (2 : 1) gave a mixture of isomeric dichlorotetratolylcyclotriphosphazatrienes (VI), m. p. 168—179° (0·9 g., 11%) (Found: C, 58·55; H, 4·9; N, 7·7; P, 15·7; Cl, 12·4. Calc. for $C_{28}H_{28}Cl_2N_3P_3$: C, 58·9; H, 4·9; N, 7·4; P, 16·3; Cl, 12·5%).

Attempted Preparation of 2,2,4,4-*Tetrachloro*-6,6-*dixylyl- and* 2,2-*Dichloro*-4,4,6,6-*tetraxylylcyclotriphosphazatrienes*.—Hexachlorocyclotriphosphazatriene (7·5 g., 0·0216 mole), aluminium chloride (5·8 g., 0·0434 mole), and dry *m*-xylene (75 ml.) were heated together in an oil-bath (160°) for 10 or 41 hr. Controlled hydrolysis was carried out in dry tetrahydrofuran (200 ml.) as previously described, and 1 g. portions of the resultant dark viscous oil were subjected to gradient-elution chromatography on pre-heated silica gel as before, with automatically mixed light petroleum–benzene and benzene–ether eluants. From the 10 hr. reaction, small

---

[26] Berlin and Butler, *Chem. Rev.*, 1960, **60**, 251; Freedman and Doak, *ibid.*, 1957, **57**, 502.

quantities of oil approximating to an isomeric mixture of the dixylyl derivative were obtained (Found: Cl, 30·8; N, 8·6. Calc. for $C_{16}H_{18}Cl_4N_3P_3$: Cl, 29·1; N, 8·6%), but despite exhaustive chromatography the only products isolated with the longer refluxing period consisted of a series of chlorine-containing resins (Found: Cl, 10·4. Calc. for $C_{32}H_{36}Cl_2N_3P_3$: Cl, 11·3%).

Chlorophenylphosphazenes.—The products obtained from the Friedel–Crafts arylation of hexachlorocyclotriphosphazatriene with chlorobenzene depend on the reaction time and activity of the aluminium chloride catalyst. The main products formed after a given time, with the same batch of aluminium chloride, are as follows:

Reaction time	Main products
42 hr.	$N_3P_3(C_6H_4Cl)Cl_5$ and $N_3P_3(C_6H_4Cl)_2Cl_4$
4 days	$N_3P_3(C_6H_4Cl)_2Cl_4$ and $N_3P_3(C_6H_4Cl)_4Cl_2$
7 days	$N_3P_3(C_6H_4Cl)_4Cl_2$ and $N_3P_3(C_6H_4Cl)_6$
11 days	Mainly $N_3P_3(C_6H_4Cl)_6$

Hexachlorocyclotriphosphazatriene (20 g., 0·0575 mole) was dissolved in dry chlorobenzene, pulverised aluminium chloride (15·3 g., 0·155 mole) was added, and the mixture was boiled under reflux for 4 days. After removal of chlorobenzene *in vacuo*, hydrolysis was achieved at 0° by adding water (14·4 ml.) in tetrahydrofuran (100 ml.). The solution was then filtered and (together with benzene washings) dried ($MgSO_4$). The solvent was removed under reduced pressure and the viscous oily residue (31 g.) was extracted with boiling light petroleum (2 × 150 ml.), leaving a brown solid (4·5 g.). The chlorophenyl derivatives were separated by column chromatography. A portion of the petroleum extract (containing *ca.* 9 g.) was diluted to 300 ml. with the same solvent and chromatographed on silica gel (45 × 3 cm.); heated at 110° for 16 hr.) prepared in light petroleum. Elution yielded, first, starting material (2·5 g., 37%) (light petroleum), then a yellow oil (2·2 g.) (light petroleum–benzene, 4 : 1) which gave after crystallisation from light petroleum 2,2,4,4-*tetrachloro*-6,6-*di*-p-*chlorophenylcyclotriphosphazatriene* (VIII), m. p. 138—139° (1·56 g., 16%) (Found: C, 28·3; H, 1·6; N, 8·7; Cl. 42·4; P, 18·6. $C_{12}H_8Cl_6N_3P_3$ requires C, 28·8; H, 1·6; N, 8·4; Cl, 42·5; P, 18·6%). With light petroleum–benzene (3 : 1) a further 1·2 g. of crystallising oil were recovered. Recrystallisation from light petroleum gave an isomeric 2,2,4,4-*tetrachloro*-6,6-*bischlorophenylcyclotriphosphazatriene* (IX), m. p. 118—120° (0·88 g., 9%) (Found: C, 28·3; H, 1·55; N, 8·5; Cl, 42·3; P, 17·8%). Finally, with light petroleum–benzene (3 : 2) an oil (1·7 g.) was obtained. When this was dissolved in light petroleum–chloroform (3 : 1) (4 ml.), 2,2-*dichloro*-4,4,6,6-*tetra*-p-*chlorophenylcyclotriphosphazatriene* (X), m. p. 189—191° (1·15 g., 9%) (Found: C, 43·2; H, 2·5; N, 6·6; Cl, 32·1; P, 13·9. $C_{24}H_{16}Cl_6N_3P_3$ requires C, 44·2; H, 2·5; N, 6·4; Cl, 32·6; P, 14·3%), slowly separated.

Other products were obtained by similar techniques with the same molar ratio (1 : 2) of hexachlorocyclotriphosphazatriene to aluminium chloride. *Pentachloro*-p-*chlorophenylcyclotriphosphazatriene* (VII) (light petroleum–benzene, 5 : 1), m. p. 88—90° (from light petroleum) (Found: C, 17·4; H, 1·1; N, 10·4; Cl, 50·7; P, 21·55. $C_6H_4Cl_6N_3P_3$ requires C, 16·7; H, 0·95; N, 9·9; Cl, 50·2; P, 21·95%), was obtained in 7% yield after a 42 hr. reaction. Similarly, after 7—11 days, *hexa*-p-*chlorophenylcyclotriphosphazatriene* (XI) (light petroleum–benzene, 1 : 1), m. p. 233–235° (from chloroform) (7%) (Found: C, 53·8; H, 2·8; N, 5·4; Cl, 26·8; P, 11·7. $C_{36}H_{24}Cl_6N_3P_3$ requires C, 53·8; H, 3·0; N, 5·2; Cl, 26·4; P, 11·6%), was isolated.

Bromophenylphosphazenes.—Hexachlorocyclotriphosphazatriene (13·1 g., 0·0375 mole) and aluminium chloride (10 g., 0·075 mole) were boiled under reflux for 6 hr. with bromobenzene (100 ml.) in an oil-bath (170°). The mixture was worked up as in the chlorobenzene experiments and a brown oil (24 g.) was obtained. As before, a portion (7·3 g.) was chromatographed in light petroleum (150 ml.) on silica gel (45 × 3 cm.; heated at 110° for 16 hr.). Elution with light petroleum gave oily fractions from which 4-bromobiphenyl, m. p. and mixed m. p. 89° (3·8 g.), crystallised. No starting material was recovered. Stepwise elution with light petroleum–benzene yielded oils, the bulk of which showed no tendency to crystallise even from solution in light petroleum. One of the oils (light petroleum–benzene, 55 : 45) crystallised, giving a very small yield of *bisbromophenyltetrachlorocyclotriphosphazatriene*, m. p. 133—135° (from light petroleum–chloroform, 4 : 1) (trace) (Found: C, 25·3; H, 1·4%; total Hal, 5·99 equiv. $C_{12}H_8Br_2Cl_4N_3P_3$ requires C, 24·45; H, 1·4%; total Hal., 6·00 equiv.). Traces of another compound, m. p. (after recrystallisation from light petroleum–benzene, 1 : 1) 170—176°, were isolated from an oil. This may be a tetrakisbromophenyl derivative.

Hydrolytic Degradation.—Experimental procedures. (*a*) Phenyl and tolyl derivatives: Samples (0·1—0·6-g.) were sealed in thick-walled glass tubes in the presence of 5 ml. of water per g. and heated under oil for the times given in the Table. For compounds (II) and (V), the water was replaced in duplicate experiments by N/20-hydrochloric acid. Diphenylphosphinic acid, m. p. 191·5—193°, was recovered from the tubes containing phenylated derivatives by quantitative transfer to a weighed (G 3) filter crucible. If the diphenyl (I) and tetraphenyl (II) derivatives are hydrolysed under the described conditions for identical times (56 hr.) the yields of diphenylphosphinic acid are 98·6% and 79·6% of the respective theoretical requirements, indicating the greater hydrolytic stability of the latter.

(*b*) Chlorophenyl derivatives: A similar procedure was adopted but with ~7 ml. N/3-aqueous potassium hydroxide for 0·25-g. samples. On cooling, the mixtures were washed with dilute potassium hydroxide solution, and the alkaline solutions were evaporated to a small volume before acidification with concentrated hydrochloric acid.

The filtrates from (*a*) and (*b*) were analysed for phosphate. The identity of most phosphonic and phosphinic acids were confirmed by mixed m. p. determinations with authentic specimens.

From the bischlorophenyl compound (IX) a new *bischlorophenylphosphinic acid*, m. p. 171—173° (from chloroform), was isolated (Found: C, 50·6; H, 3·7; Cl, 24·8; P, 10·6. $C_{12}H_9Cl_2O_2P$ requires C, 50·2; H, 3·2; Cl, 24·7; P, 10·8%).

The research reported in this paper has been made possible through the support and sponsorship of the U.S. Department of Army, through its European Research Office. We are indebted to Dr. K. Hills of this laboratory for the synthesis of the tetraphenyl derivative (II) from the diphenyl compound (I), and part of the chromatographic separation procedure, to Dr. L. Freedman, North Carolina College, for specimens of *p*-chlorophenylphosphonic and di-*p*-chlorophenylphosphinic acid, and to Dr. L. Quin of Duke University for a specimen of the *p*-toluidine *m*-chlorophenyl-*p*-chlorophenylphosphinate. A gift of 150 g. of mixed chlorocyclophosphazene oligomers from the Millmaster Chemical Corporation, New York, is acknowledged.

DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
MALET STREET, LONDON W.C.1.
[*Received, March 13th,* 1963.]