tration well below a mole fraction of 0.1, where they begin to be broken in favor of hydrogen bonds with the solvent. In the low-concentration region the NH resonance position increases rapidly with decreasing concentration. Thus, the solvent–solute hydrogen bonds do not affect the NH resonance as strongly as the ones between borate molecules (*vide infra*). This is quite reasonable since acetonitrile is only a moderately strong hydrogen-bond acceptor.[26–28]

Attempts to determine the equilibrium constant for the association process in acetonitrile were unsuccessful since the curve representing the plot of τ_{NH} against concentration becomes almost asymptotic at infinite dilution (Figure 5) and, therefore, makes the determination of an intercept or a meaningful slope impossible.

One can conclude that tris(2-methylaminoethyl) borate is a highly associated substance in the pure state at room temperature and that the association can be broken by heating the pure compound to 160° or by dissolving it in large amounts of acetonitrile. Since plots of the NH peak positions against concentration from both nmr and infrared studies show a continuous variation with no inflection in the curves, the association of borate molecules must involve *intermolecular* >N–H - - - - O< hydrogen bonds rather than intramolecular ones.

(26) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).
(27) A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 1715 (1963).
(28) W. Dannhauser and A. F. Flueckinger, *J. Phys. Chem.*, **68**, 1814 (1964).

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana

Reactions of Hexachloro- and 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatrienes with Sodium Phenoxide[1]

By E. T. McBee, K. Okuhara, and C. J. Morton

Received August 23, 1965

Treatment of hexachlorocyclotriphosphazatriene with sodium phenoxide followed by ammonolysis afforded two isomers of $P_3N_3(NH_2)_2(OC_6H_5)_4$ in comparable yields, and they were different from the third isomer obtained from an isomer of $P_3N_3(NH_2)_2Cl_4$ by phenoxylation. The three isomers of $P_3N_3(NH_2)_3(OC_6H_5)_3$ were also obtained. A similar treatment of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene afforded three isomers of $P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$, and the isomer obtained in the smallest yield was also prepared by phenoxylation of an isomer of $P_3N_3(C_6H_5)_2(NH_2)_2Cl_2$. The structures of these isomers were assigned on the basis of proton magnetic resonance spectra and chromatographic adsorption sequence. The results indicate that the substitution pattern of the phenoxylation is predominantly nongeminal with a slight *cis* preference over *trans*.

Introduction

Some patterns of successive replacements of chlorine atoms in hexachlorocyclotriphosphazatriene have been examined; hence, dimethylamine reacts by nongeminal substitution,[2–4] whereas ethylenimine,[5] potassium fluoride (or fluorosulfite),[6] and mercaptide[7] follow geminal patterns. Recently, *trans*-2,4,6-trisdimethylamino-2,4,6-triphenoxycyclotriphosphazatriene was isolated[8] in 30% yield by dimethylaminolysis of the mixture produced by phenoxylation of $P_3N_3Cl_6$. For such substitutions, evaluation of the reaction parameters is hindered since low material balances were obtained.

We have studied the reactions of hexachloro- and 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene with sodium phenoxide in acetone. Not only were the reactions found to follow a nongeminal substitution pattern, but also semiquantitative evaluations of reaction parameters were made.

Results and Discussion

Hexachlorocyclotriphosphazatriene was treated with various proportions of sodium phenoxide. The complex mixture of products after chromatographic separation gave pure only chloropentaphenoxycyclotriphosphazatriene (I), mp 69–71°, and one isomer of dichlorotetraphenoxycyclotriphosphazatriene (II), mp 75–77°. The former compound[9] and the melting point (75–76°) of the latter[10] have been reported previously.

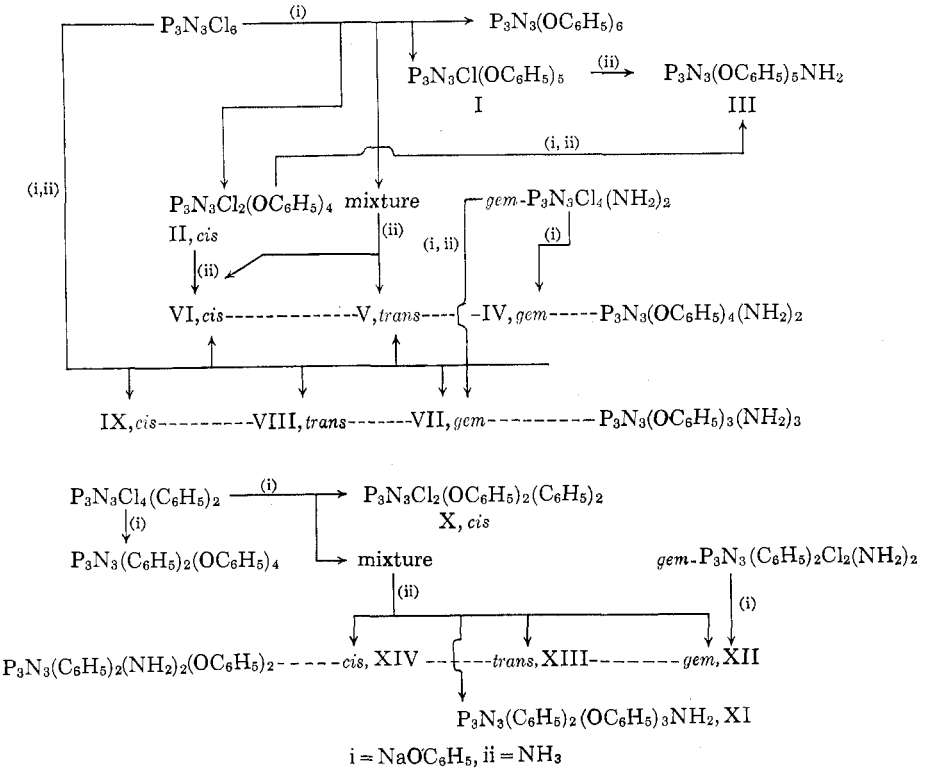
Ammonolysis of I gave aminopentaphenoxycyclotriphosphazatriene (III), which was identified by elemental analysis.

A *cis*-2,4-dichloro structure was assigned to II since

(1) This paper is based on a portion of the thesis submitted by K. Okuhara to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The research was supported in part by the Office of Ordnance Research.
(2) M. Becke-Goehring, K. John, and E. Fluck, *Z. Anorg. Allgem. Chem.*, **302**, 103 (1959).
(3) S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 872 (1961).
(4) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964).
(5) Y. Kobayashi, L. A. Chasin, and L. B. Clapp, *ibid.*, **2**, 212 (1963).
(6) A. C. Chapman, D. H. Paine, H. T. Searle, E. R. Smith, and R. F. M. White, *J. Chem. Soc.*, 1768 (1961).
(7) A. P. Carroll and R. A. Shaw, *Chem. Ind.* (London), 1908 (1962).
(8) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **4**, 419 (1965).
(9) B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, 1735 (1964).
(10) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).

SCHEME I

PHENOXYLATION OF $P_3N_3Cl_6$ AND $P_3N_3Cl_4(C_6H_5)_2$ (6,6-DIPHENYL)



ammonolysis gave the isomer of $P_3N_3(NH_2)_2(OC_6H_5)_4$ melting at 118–120° in 77% yield, which is shown later to have a similar configuration. The yields of I and II were, respectively, 71 and 0% (1:5.0), 52 and 8% (1:4.5), and 5 and 25% (1:4.0); the figures in parentheses denote the reactant mole ratio ($P_3N_3Cl_6$:NaO-C_6H_5).

When the reactant ratio was 1:5.5, hexaphenoxycyclotriphosphazatriene[9,11,12] and I were obtained in 37 and 44% yields, respectively. Chromatographic separation of these compounds from each other and of I from the isomeric mixture of tetraphenoxy compounds was not difficult. However, the latter mixture could not be further separated by chromatography although isomer II crystallized slowly from it. The crystallization became easier when such isomeric mixtures were partially ammonolyzed and the ammonolyzed products were removed by chromatography. It is not clear whether this improvement was due to preferential ammonolysis of other isomers of $P_3N_3Cl_2(OC_6H_5)_4$ or simply the removal of a small amount of $P_3N_3Cl_3(OC_6H_5)_3$ by ammonolysis.

The presence of an isomer of II among the products of this phenoxylation reaction was confirmed by ammonolysis of the reaction mixture; this reaction afforded two isomers of $P_3N_3(NH_2)_2(OC_6H_5)_4$ (V and VI) and three isomers of $P_3N_3(NH_2)_3(OC_6H_5)_3$ (VII, VIII, and IX).

The third isomer of $P_3N_2(NH_2)_2(OC_6H_5)_4$ (IV) was obtained by phenoxylation of a previously isolated[13] isomer of $P_3N_3(NH_2)_2Cl_4$. The latter compound was also converted to VII by the sequence

$$P_3N_3(NH_2)_2Cl_4 \xrightarrow{NaOC_6H_5} [P_3N_3(NH_2)_2Cl(OC_6H_5)_3] \xrightarrow{NH_3} P_3N_3(NH_2)_3(OC_6H_5)_3$$

Reaction conditions, yields, and structural assignments for the compounds IV–IX are given in Table I.

TABLE I

ISOMERS OF $P_3N_3(NH_2)_2(OC_6H_5)_4$ AND $P_3N_3(NH_2)_3(OC_6H_5)_3$

Compd no.	Mp, °C	Structure	Yield (%) from $P_3N_3Cl_6$ a	b	c	$P_3N_3(NH_2)_2Cl_4$
IV	104–106	2,2-Diamino	0	0	0	84[d]
V	110–111.5	*trans*-2,4-Diamino	3	10	28	
VI	118–120	*cis*-2,4-Diamino	4	12	34	
VII	135.5–137	2,2,4-Triamino	6	3	0	50[d]
VIII	210–212	*trans*-2,4,6-Triamino	12	23	6	
IX	189–190	*cis*-2,4,6-Triamino	9	4	(1)	

[a,b,c] Treatment with sodium phenoxide in 1:2, 1:3, and 1:4 ratios, respectively, followed by ammonolysis. [d] Treatment with excess sodium phenoxide.

In a similar way, 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene was treated with sodium phenoxide, and the resultant mixture was divided into two equal portions. One of these gave an isomer of $P_3N_3(C_6H_5)_2Cl_2(OC_6H_5)_2$ (X) in 25% yield. The other gave a crude crystalline fraction of X and an oily fraction. The former fraction after ammonolysis gave an isomer of $P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$ (XIV). The latter

(11) B. W. Fitzsimmons and R. A. Shaw, *Chem. Ind.* (London), 109 (1961).

(12) E. T. McBee and P. Johncock, unpublished results, quoted by C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 350 (1962).

(13) A. M. de Ficquelmont, *Ann. Chim.*, **12**, 169 (1939).

fraction was also ammonolyzed, and chromatographic separation of the product mixture afforded 2-amino-2,4,-4-triphenoxy-6,6-diphenyltriphosphazatriene (XI) and three isomers of $P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$ (XII XIII, and XIV). The combined yields and other data for these isomers are given in Table II. Compound XI was identified by elemental analysis, and XII was also obtained by phenoxylation of the previously isolated[14,15] isomer of $P_3N_3(C_6H_5)_2(NH_2)_2Cl_2$ (6,6-diphenyl).

TABLE II

ISOMERS OF $P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$ (6,6-DIPHENYL)

Compd no.	Mp, °C	Structure	Yield (%) from $P_3N_3(C_6H_5)_2Cl_4$[a]	Yield (%) from $P_3N_3(C_6H_5)_2(NH_2)_2Cl$
XII	150–152	2,2-Diamino	4.5	71[b]
XIII	161–163	*trans*-2,4-Diamino	33.2	
XIV	156–157.5	*cis*-2,4-Diamino	39.4	

[a] See footnote *a* of Table I. [b] See footnote *d* of Table I.

Treatment of $P_3N_3(C_6H_5)_2Cl_4$ with excess sodium phenoxide gave the 2,2,4-4-tetraphenoxy-6,6-diphenyl compound.

Analytical data for I–XIV are given in Table III. The structures assigned to compounds IV–IX and XII–XIV were made on the basis of proton magnetic resonance spectra and chromatographic adsorption sequence. The chemical shifts of the amino protons measured in three solvents are given in Table IV. The shifts for IV, VII, and XII are noticeably different from those of the other compounds and are similar to those of 2,2-diamino-4,4,6,6-tetraphenylcyclotriphosphazatriene (XV), prepared by ammonolysis of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene.[16] For this and subsequent reasons, a geminal diamino configuration was assigned to IV, VII, and XII. Hence, it follows that their precursors—the known[13–15] isomers of $P_3N_3(NH_2)_2Cl_4$ and $P_3N_3(C_6H_5)_2(NH_2)_2Cl_2$—also have geminal diamino configurations.

Differentiation of the *cis* and *trans* isomers of 2,4-diamino-2,4-diphenoxy-6,6-diphenylcyclotriphosphazatriene (XIII and XIV) was made by detection of equivalence or nonequivalence of the two phenyl groups by a detailed study of the shapes of phenyl proton resonance signals as described below.[17] In principle, only the *cis* isomer has nonequivalent phenyl groups.

The proton magnetic resonance spectrum of 2,-2-diamino-4,4,6,6-tetraphenylcyclotriphosphazatriene[16] (XV) is given in Figure 1 with the main peaks numbered for convenience. The area ratio (2.00:3.05) indicates that peaks 1–8 are due to the *ortho* hydrogens and peaks 9–13 are due to *para* and *meta* hydrogens. It was found that phenyl proton magnetic resonance spectra of many 6,6-diphenylcyclotriphosphazatrienes can be classified into two types. In a spectrum of one type, a peak corresponding to each of the peaks 1–13 is easily found since the relative position and intensity of each peak within peaks 1–8 or within peaks 9–13 seem unchanged from compound to compound. Actually the spread of peaks 1–8 and that of peaks 9–13 are almost constant, that is, 23 and 9 cps, respectively, whereas the distance between peaks 8 and 9 varies. This is because the multiplicity of the peaks is due to coupling between protons within a single phenyl group and possibly to coupling between protons and phosphorus nuclei, and the chemical shift between *ortho* protons and that of the *meta* (*para*) proton is generally not constant. A compound showing such a phenyl proton resonance spectrum was generally interpreted as possessing two equivalent phenyl groups. A compound

(14) H. Bode, K. Butow, and G. Lienau, *Ber.*, **81**, 547 (1948).
(15) M. Becke-Goehring and K. John, *Z. Anorg. Allgem. Chem.*, **304**, 126 (1960).
(16) Prepared for publication.
(17) Dr. Gushkin informs us that the same argument was used to differentiate *cis*- and *trans*-$P_3N_3Cl_2(C_6H_5)_4$.

TABLE III

ELEMENTAL ANALYSIS DATA[a]

Formula and compd no.	% C	H	N	P	Cl
$P_3N_3Cl(OC_6H_5)_5$			6.61		5.58
I			6.45		5.19
$P_3N_3Cl_2(OC_6H_5)_4$	49.84	3.49	7.27	16.08	12.27
II	50.49	3.87	7.04	15.38	12.20
$P_3N_3(NH_2)(OC_6H_5)_5$	58.45	4.42	9.09	15.07	
III	58.20	4.45	9.24	14.80	
$P_3N_3(NH_2)_2(OC_6H_5)_4$	53.44	4.49	12.99	17.23	
IV	53.86	5.05	13.32	17.40	
V	53.42	4.27	13.11	17.45	
VI	53.80	4.46	12.79	17.52	
$P_3N_3(NH_2)_3(OC_6H_5)_3$	46.76	4.58	18.18	20.10	
VII	47.70	5.22	18.08	19.32	
VIII	46.78	4.18	18.44	20.07	
IX	46.66	4.80	18.00	20.02	
$P_3N_3(C_6H_5)_2Cl_2(OC_6H_5)_2$	52.76	3.69	7.69	17.02	12.98
X	52.30	3.78	7.71	16.72	12.87
$P_3N_3(C_6H_5)_2(NH_2)(OC_6H_5)_3$	61.65	4.66	9.59	15.90	
XI	61.79	4.87	9.79	15.57	
$P_3N_3(C_6H_5)_3(NH_2)_2(OC_6H_5)_2$	56.81	4.77	13.80	18.31	
XII	56.62	5.08	13.90	18.20	
XIII	56.61	4.96	13.87	18.01	
XIV	56.61	5.09	13.81	17.99	

[a] The figures on the line where a formula is written represent the calculated values.

TABLE IV

CHEMICAL SHIFT OF AMIDO PROTON RESONANCE

Formula	Chemical shift, ppm[a] Geminal	*trans*	*cis*
$P_3N_3(C_6H_5)_4(NH_2)_2$	XV		
	2.75		
	3.63		
	4.34		
$P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$	XII	XIII	XIV
	2.48	2.82	3.15
	3.6	4.26	4.37
	4.49	4.92	4.95
$P_3N_3(NH_2)_2(OC_6H_5)_4$	IV	V	VII
	2.21	2.55	2.94
	3.65	4.42	4.47
	4.45	4.94[b]	4.95[b]
$P_3N_3(NH_2)_3(OC_6H_5)_3$	VII	VIII	IX
	2.5[b]	...	...
	3.4[c]	4.00	4.19
	4.42	4.80	4.90

[a] Taken downfield relative to internal tetramethylsilane. For each compound: the first figure, in $CDCl_3$; the second, in dimethylformamide; the third, in pyridine. [b] Broad. [c] Additional peak (?) at 4.19.

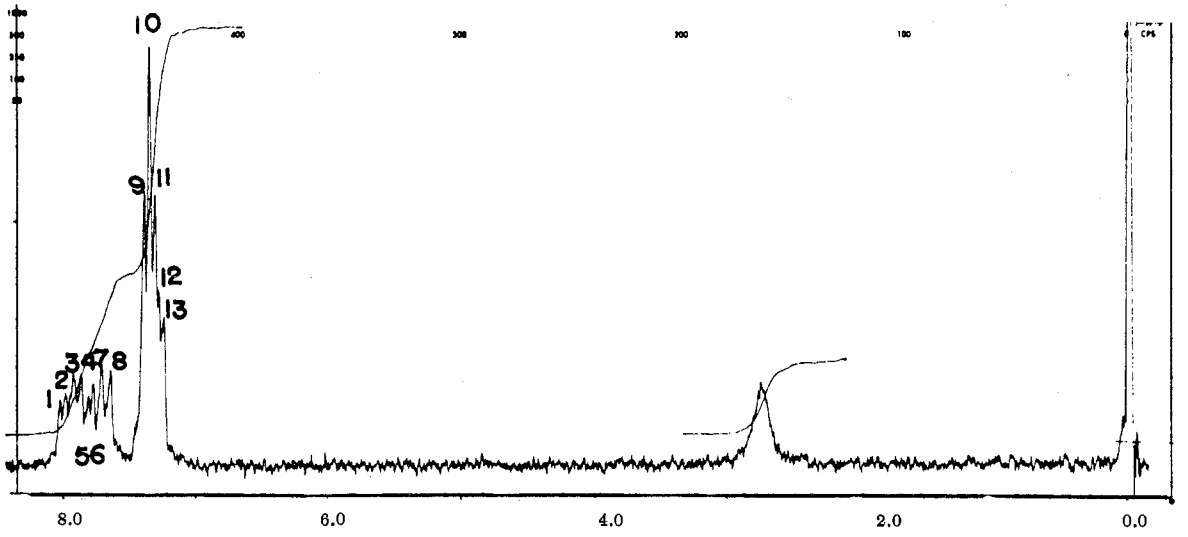


Figure 1.—H^1 nmr spectrum (ppm) of $P_3N_3(C_6H_5)_4(NH_2)_2$ (XV).

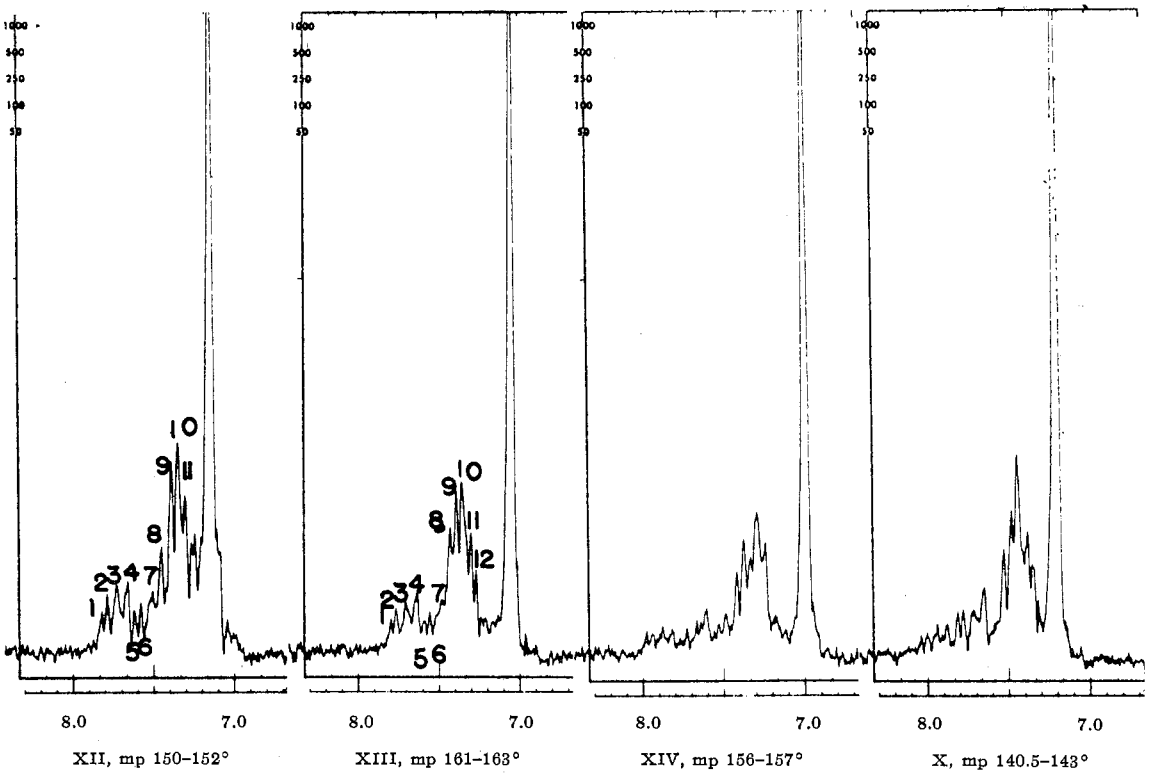


Figure 2.—H^1 nmr spectra (ppm) of $P_3N_3(C_6H_5)_2Cl_2(OC_6H_5)_2$ (X) and $P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$ (XII, XIII, and XIV).

whose spectrum differed from the above type was interpreted as possessing two nonequivalent phenyl groups. In compounds of the latter type, the resultant spectrum is comprised of two different phenyl proton resonances and is expected to be more complex. In agreement with this interpretation, compounds of the type $P_3N_3(C_6H_5)_2A_3B$ (6,6-diphenyl) showed the latter type of spectrum.

The phenyl proton resonance spectra of $P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$ and $P_3N_3(C_6H_5)_2Cl_2(OC_6H_5)_2$ are given in Figure 2. According to the above argument it can be seen that XIV and X have nonequivalent phenyl groups and thus have, respectively, *cis*-diamino and *cis*-dichloro configurations.

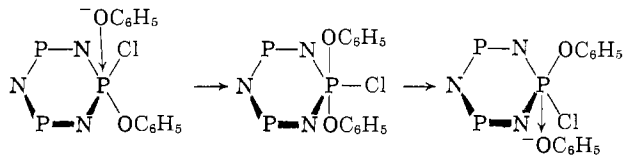
Among the isomers of $P_3N_3(NH_2)_2(OC_6H_5)_4$, VI showed the most complicated proton resonance spectrum of phenoxy groups, and this situation may be expected for the *cis* structure. A successful argument for this assignment, however, could not be made on this basis since each of the other two isomers showed only a single phenoxy resonance peak; the exact condition of the above splitting could not be understood. The assignment of the *cis* and *trans* structures to $P_3N_3(NH_2)_2(OC_6H_5)_4$ and $P_3N_3(NH_2)_3(OC_6H_5)_3$ was based on chromatographic adsorption (or elution) sequence. However, it should be emphasized that, even in the absence of other evidence, differentiation between the *cis* and *trans* isomers of $P_3N_3(NH_2)_2(OC_6H_5)_4$ can be made on the basis of correlations present in Table IV.

The main difference of adsorption behavior between

cis and *trans* isomers of $P_3N_3(NH_2)_2(OC_6H_5)_4$ is a function of their relative polarities. In the *trans* isomer, the groups on each side of the ring are arranged identically. The adsorption of one side, existing in equilibrium with that of the other side, has a strength (energy) equal to the *average* value for the molecule. In the *cis* isomer, the adsorption of the side to which one phenoxy and two amino groups are attached is preferred since it is more basic and less sterically hindered. As a result, the adsorption of this side occurs predominantly in the equilibrium with the adsorption of the other side of the *cis* isomer. Hence, the average energy of adsorption for the molecule is greater than that of the middle state, where both sides are adsorbed equally. Since this middle state is essentially equal to the situation encountered by the *trans* compound, the *cis* isomer is expected to be more strongly adsorbed. By similar kinds of argument, generally, a *cis* isomer (or a geminal isomer) is expected to be adsorbed more strongly than the corresponding *trans* isomer for the cyclotriphosphazatrienes of the types $P_3N_3A_2B_4$, $P_3N_3A_3B_3$, and $P_3N_3A_2B_2C_2$ (fixed geminal C's).

From the order of elution, adsorption of isomers of $P_3N_3(NH_2)_2(OC_6H_5)_4$ and $P_3N_3(NH_2)_3(OC_6H_5)_3$ was found to increase in the order V < VI < VIII < VII < IX, and thus identification of *trans* and *cis* isomers was made as given in Table I. For $P_3N_3(C_6H_5)_2(NH_2)_2(OC_6H_5)_2$ isomers, the order of adsorption was *trans* < *cis* < *gem*.

The possibility of inversion of configuration around a phosphorus carrying Cl and OC_6H_5 was conceived as occurring by the process



Hence, *cis*-2,4-dichloro-2,4,6,6-tetraphenoxycyclotriphosphazatriene (X) was treated with sodium phenoxide, the resulting mixture was ammonolyzed, and the products were examined. Only (III) aminopentaphenoxy- and (VI) *cis*-2,4-diamino-2,4,6,6-tetraphenoxycyclotriphosphazatrienes were found; the *trans*-2,4-diamino isomer (V) was not detected though carefully sought. The complete or almost complete absence of isomerization might be explained by front-side attack of a phenoxide ion both for the phenoxylation and for the possible phenoxide exchange. Bailey and Parker[18a] suggested front-side attack for a reaction of hexachlorocyclotriphosphazatriene. However, back-side attack (inversion of configuration)[18b] of a reagent is much more likely as the general steric course of nucleophilic substitution reactions of cyclotriphosphazatrienes in view of the many established examples in phosphorylation[19] and in reactions of carbon compounds.[20] If the inversion of configuration during the substitutions is assumed, the absence of isomerization indicates that displacement of a phenoxide ion is much more difficult than displacement of a chloride ion, and this seems to reflect easier partial bond breaking in P–Cl than in P–O–. Thus, the importance of the bond-breaking step in SN2 reactions of cyclotriphosphazatrienes is suggested.

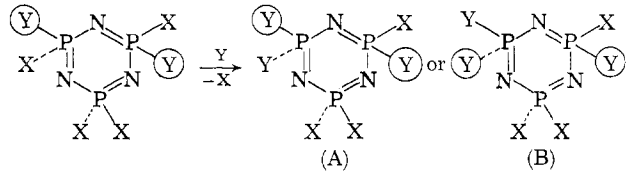
A semiquantitative discussion of a substitution pattern may best be made in terms of partial rate factors, a concept often used for benzene derivatives.[21–24] The partial rate factor g_f is defined as the ratio of the rate of the geminal substitution, k_g, to the rate of the monosubstitution, k_m, with each rate constant referring to one reaction site. Similarly, the partial rate factors t_f and c_f are defined as k_t/k_m and k_c/k_m, respectively. If additivity of substituent effect on free energy of activation is assumed, the relative rate of any step in the homologous series is expressed as a product of partial rate factors. However, for some steps of homologous substitution reactions of cyclotriphosphazatrienes, the rate expressions with partial rate factors are dependent on the assumed steric course whereas in benzene derivatives the rate expressions are always unequivocal. For the following example, for instance, the theoretical relative rate is $2g_fc_f$ if the configuration is retained (A) or $2g_ft_f$ if the configuration is inverted (B).

$$P_3N_3X_6 + Y \xrightarrow{6k_m} P_3N_3X_5Y + X$$

$$P_3N_3X_5Y + Y \xrightarrow{k_g} \textit{gem}\text{-}P_3N_3X_4Y_2 + X$$

$$P_3N_3X_5Y + Y \xrightarrow{2k_t} \textit{trans}\text{-}P_3N_3X_4Y_2 + X$$

$$P_3N_3X_5Y + Y \xrightarrow{2k_c} \textit{cis}\text{-}P_3N_3X_4Y_2 + X$$



Ratios of geminal, *trans*, and *cis* isomers of $P_3N_3(C_6H_5)_2Cl_2(OC_6H_5)_2$ isolated as ammonolysis product are approximately 1:7.4:8.8 as shown in Table II. Under the assumption of additivity of substituent effect, the theoretical relative rates of formation of the geminal, *trans*, and *cis* isomers are $c_f't_f'g_f$, $c_f't_f't_f$, and $c_f't_f'c_f$, respectively, where a plain partial rate factor refers to a phenoxy group as substituent, and a partial rate factor having a prime refers to a phenyl group as substituent. Thus, neglecting change of ratios of the isomers of $P_3N_3(C_6H_5)_2Cl_2(OC_6H_5)_2$ by further substitution into $P_3N_3(C_6H_5)_2Cl(OC_6H_5)_3$, the ratios $g_f:t_f:c_f$ are 1:7.4:8.8. From these ratios the relative reactivities of isomers having the same n value for $P_3N_3Cl_n$-

(18) (a) J. V. Bailey and R. E. Parker, *Chem. Ind.* (London), 1823 (1962); (b) N. L. Paddock, *Quart. Rev.* (London), **18**, 168 (1964).
(19) R. F. Hudson, *Advan. Inorg. Chem. Radiochem.*, **5**, 357 (1963).
(20) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 115–119; or see, for example, A. J. H. Houssa, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 1700 (1929).
(21) C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward, *ibid.*, 1959 (1931).
(22) F. E. Condon, *J. Am. Chem. Soc.*, **70**, 1963 (1948).
(23) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2310 (1955).
(24) H. C. Brown and L. M. Stock, *ibid.*, **79**, 1421 (1957).

$(OC_6H_5)_{6-n}$ (n = 2, 3, or 4) and the isomer distribution of $P_3N_3Cl_n(OC_6H_5)_{6-n}$ to be obtained from any compound of $P_3N_3Cl_{n+1}(OC_6H_5)_{5-n}$ (n = 2, 3, or 4) can be calculated.

The ratios of geminal, *trans*, and *cis* isomers of $P_3N_3Cl_4(OC_6H_5)_2$ to be obtained from $P_3N_3Cl_5(OC_6H_5)$ (at a low conversion) are theoretically $1:2 \times 7.4:2 \times 8.8$ if the above partial rate factor ratios are correct; in other words, 3, 44, and 53% of the products are the geminal, *trans*, and *cis* isomers, respectively. The same isomer distribution of $P_3N_3Cl_4(OC_6H_5)_2$ should be obtained from $P_3N_3Cl_6$ by successive replacements of chlorine atoms by phenoxide groups if all of the starting material could be disubstituted without further substitution or loss. Such hypothetical isomer distribution can also be calculated for $P_3N_3Cl_3(OC_6H_5)_3$.

$$\text{2,2,4-trichloro} = 3\% + 44\% \frac{2g_f t_f}{2g_f t_f + 2c_f t_f} + 53\% \frac{2c_f g_f}{2c_f g_f + t_f t_f + c_f c_f} =$$

$$3\% + 44\%(0.10) + 53\%(0.12) = 14\%$$

$$\textit{trans}\text{-2,4,6-trichloro} = 44\%(0.90) + 53\%(0.36) = 59\%$$

$$\textit{cis}\text{-2,4,6-trichloro} = 53\%(0.52) = 27\%$$

and for $P_3N_3Cl_2(OC_6H_5)_4$

$$\text{2,2-dichloro} = 14\%(0.06) = 0.8\%$$

$$\textit{trans}\text{-2,4-dichloro} = 14\%(0.43) + 59\%(0.70) = 47\%$$

$$\textit{cis}\text{-2,4-dichloro} = 14\%(0.51) + 59\%(0.30) + 27\% =$$

$$52\% = 14\% \frac{g_f c_f t_f}{g_f c_f t_f + c_f t_f t_f + c_f c_f t_f} + 59\% \frac{2g_f c_f t_f}{2g_f c_f t_f + g_f t_f t_f} + 27\%$$

under the assumption of inversion of configuration during the substitutions.

Comparing the calculated values with the yields, given in Table I, of the corresponding aminophenoxy compounds, one may understand why the geminal isomer of $P_3N_3(NH_2)_2(OC_6H_5)_4$ could not be detected. Relatively large yields of the 2,2,4-triamino derivative and larger yields of *cis* isomer of $P_3N_3(NH_2)_2(OC_6H_5)_2$ over the *trans* isomer can also be explained although it is not understood why c_f is greater than t_f.

Experimental Section

All melting points are uncorrected. Modified preparations of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene are described in a separate paper.[25] A solution of sodium phenoxide in acetone was prepared, *in situ*, by addition of an equivalent amount of sodium to a solution of phenol in acetone dried with magnesium sulfate. The detailed procedure of exhaustive ammonolysis is already described.[16]

Chloropentaphenoxycyclotriphosphazatriene (I).—A solution of hexachlorocyclotriphosphazatriene (5.00 g, 0.0144 mole) in acetone (80 ml) was added over a 25-min period to a stirred solution of sodium phenoxide (0.0800 mole) in acetone (120 ml) cooled externally with water. The resulting mixture was stirred for 21 hr without cooling, and then the acetone was distilled off under reduced pressure. The pasty residue was treated with ether and water, and the ether layer was washed with 0.1 *N* sodium hydroxide, dried, and evaporated. The remaining syrup partially crystallized, and hexaphenoxycyclotriphosphazatriene (2.71 g), mp 110–111.5°, was collected by digesting with a minimum amount of ether followed by filtration. Recrystallization from acetone–hexane gave a pure sample, mp 111–112°, which was identified by undepressed mixture melting point with an authentic sample[12] (lit.[9,12] mp 110–111°). The oil (5.7 g) recovered from the filtrate was chromatographed on acid-washed alumina (160 g). Elution with 3:7 benzene–hexane afforded I (4.07 g, 0.00640 mole, 44.5%), mp 67–69.5°, and elution with 1:1 benzene–hexane gave an additional amount (1.03 g) of the hexaphenoxy compound, increasing the total yield to 3.71 g (0.00540 mole, 37.4%). Compound I was recrystallized from ether–hexane, and the melting point increased to 69–71° (lit[9] mp 67–68°).

***cis*-2,4-Dichloro-2,4,6,6-tetraphenoxycyclotriphosphazatriene** (II).—A solution of hexachlorocyclotriphosphazatriene (20.00 g, 0.0576 mole) in acetone (200 ml) was added over 5 min to a stirred solution of sodium phenoxide (0.230 mole) in acetone (400 ml) cooled with ice. The resulting mixture was stirred for 36 hr without cooling, and then the acetone was distilled off under reduced pressure. Ether and water were added to the residue; the ether layer was separated, washed with water, dried, and evaporated. The remaining oil was dissolved in 1:9 benzene–hexane and passed through a column of acid-washed alumina (100 g). The eluate was dissolved in ether (300 ml), and ammonia gas was bubbled through the solution for 24 hr. The resulting mixture was poured onto water, the chloride ion in the aqueous layer was determined as AgCl (2.77 g, 0.0194 mole), and the oil (28.2 g) was obtained from the ether layer chromatographed on acid-washed alumina (900 g). Elution with 2:3 benzene–hexane afforded oils (2.63 g) and crude mixtures (15.26 g), from which the tetraphenoxycyclotriphosphazatriene crystallized. From the latter, II, 8.44 g (0.0146 mole, 25%), mp 68–72°, was obtained. Recrystallization from hexane containing a small amount of ether afforded prisms, mp 75–77° (cited[9] mp 75–76°). Elution with benzene gave a total 1.83 g (0.00288 mole, 5.0%) of I, mp 65–69°, and elution with 3:97 methanol–benzene gave a mixture (6.95 g) of aminolyzed products.

***trans*- and *cis*-2,4-Diamino-2,4,6,6-tetraphenoxycyclotriphosphazatriene (V and VI).**—Hexachlorocyclotriphosphazatriene (20.00 g, 0.0576 mole) was treated with sodium phenoxide (0.230 mole) in the same way as described in the preceding section. The resulting crude oil was chromatographed on acid-washed alumina (700 g) and separated into three fractions containing: (i) 29.32 g, (ii) 0.90 g, and (iii) chloropentaphenoxycyclotriphosphazatriene (I), 2.15 g.

The first fraction was dissolved in ether (80 ml), and the solution was left standing with liquid ammonia (*ca.* 100 ml) in an autoclave for 4 days. The resulting mixture was filtered, giving a precipitate that was Soxhlet-extracted with ether for 1 day; the *cis*-2,4-diamino compound (VI) (6.75 g), mp 113–117°, was obtained from the extract. The precipitate still remaining in the thimble was extracted with ether for another 2 days and was then poured onto water; *trans*-2,4,6-triamino-2,4,6-triphenoxycyclotriphosphazatriene (VIII) (1.10 g), mp 207–211°, was filtered off. An additional amount (0.40 g) of VIII was obtained from the second ether extract, together with a small amount (0.26 g) of an impure sample of the corresponding *cis* isomer (IX). The material recovered from the filtrate of the ammonolysis mixture was chromatographed on acid-washed alumina (330 g). The *trans*-2,4-diamino compound (V) (9.3 g, mp 107–110°) was eluted with 1:9 and 1:4 ether–benzene, and VI (4.5 g, mp 117–119°) was eluted with 1:1 ether–benzene. The *trans* isomer (V) was recrystallized from benzene; crystals obtained in this way seemed to contain benzene and showed a sharp melting point (110–111.5°) only after complete drying. The *cis* isomer (VI) was recrystallized from ethanol, and the melting point was increased to 118–120°. The yields of the products are summarized as follows: V, 28% (9.3 g, 0.0161 mole); VI, 34% (11.25 g, 0.0194

(25) E. T. McBee, K. Okuhara, and C. J. Morton, *Inorg. Chem.*, **4**, 1672 (1965).

mole); VIII, 6% (1.50 g, 0.0032 mole); IX, 1% (0.26 g, 0.0006 mole).

2,2-Diamino-4,4,6,6-tetraphenoxycyclotriphosphazatriene (IV).—A solution of 2,2-diamino-4,4,6,6-tetrachlorocyclotriphosphazatriene (5.00 g, 0.0162 mole; mp 162–164°) in acetone (90 ml) was added to a solution of sodium phenoxide (0.0800 mole) in acetone (150 ml), and the resulting mixture was stirred for 67 hr at room temperature. The oil obtained after workup crystallized overnight and afforded IV (6.30 g, 0.0136 mole, 84%), mp 96–100°. Samples recrystallized from hexane–benzene had mp 102–104°, which was increased to 104–106° by column chromatography on acid-washed alumina.

Triaminotriphenoxycyclotriphosphazatrienes (VII, VIII, and IX).—Hexachlorocyclotriphosphazatriene (20.00 g, 0.0576 mole) was treated with sodium phenoxide (0.173 mole) in acetone, and an oil (26.4 g) was obtained after workup. The ether solution of the oil was left standing with liquid ammonia in an autoclave for 4 days; the resulting mixture was filtered, and evaporation of the filtrate gave an oil (11.15 g).

The precipitate was extracted with ether for 1 day and with benzene for another day. The material still remaining in the extraction thimble was poured onto water, and a powder (8.77 g, melting mostly at 170–205°) was filtered off. Elaborate fractional recrystallization (from ethanol or more satisfactorily from dioxane) of the powder and the materials obtained from the extracts afforded the *trans*-2,4,6-triamino compound (VIII) (6.47 g), mp 210–212°, and the *cis*-2,4,6-triamino compound (IX) (0.85 g), mp 186.5–189°. Analytical samples of VIII and IX were obtained after recrystallization from ethanol and melted at 210–212° and at 189–190°, respectively.

The above-mentioned oil (11.15 g) and the oil (0.49 g) obtained in the above recrystallization procedures were combined and chromatographed on acid-washed alumina (408 g). The following compounds were obtained: *trans*-2,4-diamino-2,4,6,6-tetraphenoxycyclotriphosphazatriene (V), mp 110–111.5° (3.22 g, 0.00595 mole, 10.3%), the corresponding *cis*-diamino compound (VI), mp 118–120° (3.83 g, 0.00708 mole, 12.3%), and the 2,2,4-triamino compound (VII), mp 135.5–137° (0.83 g, 0.00180 mole, 3.1%). The melting points of the purified samples and crude yields based on the weights of the corresponding chromatographic fractions are given above. Compound VII was recrystallized from ethanol for the analytical sample. Small amounts of VIII (0.10 g) and IX (0.25 g) were also obtained, and the total yields of VIII and IX were increased to 24.6% (6.57 g, 0.0142 mole) and to 4.1% (1.10 g, 0.00238 mole), respectively. The chromatographic data are given in Table V.

Table V

Fraction		Solvent	Total vol, ml	Eluate, g	Remarks
1–3	1:9	ether–benzene	450	0.48	Light oil
4–11	1:9	ether–benzene	800	Trace	
12–18	3:17	ether–benzene	800	Trace	
19–28	1:4	ether–benzene	1300	3.22	V
29–35	3:7	ether–benzene	600	0.43	Oil
36–42	1:1	ether–benzene	1700	3.83	VI
43	1:1	ether–benzene	300	0.19	Oil
44–46		Ether	300	0.20	Oil
47–49		Ether	600	Trace	
50		Ether	400	0.10	VIII
51		Ether	350	Trace	
52–58	1:9	ethanol–ether	1100	Trace	
59–60		Methanol	200	0.83	VII
61		Methanol	100	0.20	Mixture
62–63		Methanol	400	0.25	IX
64–65		Methanol	1500	Trace	

Aminopentaphenoxycyclotriphosphazatriene (III).—A solution of I (3.90 g, 0.0061 mole) in ether (80 ml) was left standing with liquid ammonia (*ca.* 80 ml) in an autoclave for 4 days at room temperature. The oil obtained after workup did not crystallize on standing for several months and was chromatographed. The first crystals appeared in a fraction after only 1 month. The remaining fractions crystallized slowly upon seeding in the presence of hexane. Crystals obtained from the first fractions melted at 57–59°, and those obtained from the last fractions melted at 64–67°. They did not depress the melting point upon admixture. These samples melted at 66–67° after being stored in sample bottles for about 2 years. They were dissolved in ether, diluted with an equal volume of hexane, and the solution was left standing in an open flask with seeding. Compound III, mp 65–67°, was deposited as prisms in 1 day and filtered off.

***cis*-2,4-Diamino-2,4,6,6-tetraphenoxycyclotriphosphazatriene (VI) from II.**—A solution of II (3.90 g, 0.00674 mole) in ether (80 ml) was left standing with liquid ammonia (*ca.* 100 ml) for 4 days at room temperature, the resulting mixture was poured onto water, more ether was added, and the ether layer was separated. The solution was dried and evaporated leaving VI, mp 115–117° (2.76 g, 0.00512 mole, 76%). An analytical sample was obtained by recrystallization from ethanol and melted at 118–120°.

2,2,4-Triamino-4,6,6-triphenoxycyclotriphosphazatriene (VII).—A solution of 2,2-diamino-4,4,6,6-tetrachlorocyclotriphosphazatriene (8.0 g, 0.0259 mole) in acetone (100 ml) was added to a solution of sodium phenoxide (0.078 mole) in acetone (200 ml), and the resulting mixture was stirred for 24 hr. The oil obtained after workup was dissolved in ether (80 ml), and the solution was left standing with liquid ammonia (*ca.* 100 ml) in an autoclave for 4 days. The resulting mixture was poured onto water, more ether was added, and a powder (7.5 g) was filtered off. The powder was recrystallized from ethanol after removal of a small amount of benzene-insoluble material giving crude VII (4.9 g, mp 133–135.5°; 1.5 g, mp 130–133.5°). An additional amount (0.85 g, mp 134–136°) of this compound was obtained from the above ether solution, increasing the total yield to 60% (7.25 g, 0.0157 mole). They did not depress melting points upon admixture with the sample (mp 135.5–137°) obtained by the other route.

***cis*-2,4-Dichloro-2,4-diphenoxy-6,6-diphenylcyclotriphosphazatriene (X).**—A solution of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene (40.00 g, 0.0928 mole; mp 93–95.5°) in acetone (200 ml) was added over a period of a few minutes to a stirred solution of sodium phenoxide (0.1856 mole) in acetone (450 ml) cooled with ice. The resulting mixture was stirred for 1 hr with ice cooling and then for 23 hr without cooling. The acetone was distilled under reduced pressure, ether and water were added to the residue, and the ether layer was separated. The aqueous layer was extracted once with ether, and the combined ether solution was divided into two equal parts. Each was dried and removal of the solvent gave slurries.

One slurry was treated with ether and the resultant crystals (4.9 g), mp 130–141°, gave X (3.8 g), mp 138–140°, after recrystallization from ethanol–benzene. An analytical sample of X was obtained after further recrystallization from a small amount of benzene and melted at 140.5–143°. The materials recovered from the filtrate and from the mother liquor were combined and chromatographed on acid-washed alumina. The first fractions (12.5 g) partially crystallized, and an additional amount (2.46 g, mp 131–141°) of X was collected, increasing the total yield to 25% (6.26 g, 0.0115 mole).

Diaminodiphenoxy-6,6-diphenylcyclotriphosphazatrienes (XII, XIII, and XIV).—From the other slurry described in the preceding section a crystalline powder (7.1 g, mp 130–140°) and an oil (18 g) were separated, and each was then ammonolyzed. The crystalline powder was left standing with a mixture of ether (80 ml) and liquid ammonia (*ca.* 100 ml) in an autoclave for 4 days. The resulting mixture was treated with benzene and water, and moderately pure *cis*-2,4-diamino-2,4-diphenoxy-6,6-diphenylcyclotriphosphazatriene (XIV) (4.8 g), mp 151–155°, was filtered off. An additional amount (1.40 g, mp 151–155°) of XIV was obtained from the benzene layer.

The earlier described oil (18 g) was similarly ammonolyzed, and recrystallization (from ethanol) of crystalline powders obtained from the water-insoluble portion of the product afforded *trans*-2,4-diamino-2,4-diphenoxy-6,6-diphenylcyclotriphosphazatri-

ene (XIII) (2.1 g, mp 160–162°; 2.5 g, mp 157–160°). The rest (11.5 g) of the water-insoluble products were combined and chromatographed on acid-washed alumina (462 g). From fractions 22–32, pure XIII (2.3 g), mp 157–160°, was obtained, and fractions 39–59 gave XIV (3.1 g), mp 152–155°. Fractions 60–62 crystallized overnight and afforded, after recrystallization from ethanol, 2,2-diamino-4,4-diphenoxy-6,6-diphenylcyclotriphosphazatriene (XII), mp 150–152°, which did not depress the melting point upon admixture with a sample prepared by the other route, described in the following section. Fractions 13–20 crystallized 4 months later, and 2-amino-2,4,4-triphenoxy-6,6-diphenylcyclotriphosphazatriene (XI) (1.25 g), mp 79–83°, was collected. A sample was dissolved in ether, and the solution was diluted with an equal volume of hexane and left standing in an open flask with seeding to give 0.7 g of prisms, mp 93–95°. An analytical sample of XI, obtained after one more recrystallization, melted at 93.5–95.5°.

TABLE VI

Fraction	Solvent	Total vol, ml	Eluate, g	Remarks
1–9	Benzene	1320	Trace	
10–11	1:4 ether–benzene	230	0.08	Light oil
12–21	1:4 ether–benzene	1230	2.06	XI
22	1:4 ether–benzene	70	0.20	XIII
23–32	2:3 ether–benzene	1200	3.03	XIII
33–38	3:2 ether–benzene	590	0.16	oil
39–49	3:2 ether–benzene	1100	1.64	XIV
50–54	4:1 ether–benzene	500	0.79	XIV
55–59	Ether	730	0.69	XIV
60–62	Methanol	200	1.06	XII
63–64	Methanol	400	Trace	

The total yields of the aminophenoxy compounds based on the starting 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene are summarized as follows: XI, 4.6% (1.25 g, 0.00214 mole); XII, 4.5% (1.06 g, 0.00209 mole); XIII, 33.2% (7.8 g, 0.0154 mole); XIV, 39.4% (9.3 g, 0.0183 mole).

2,2-Diamino-4,4-diphenoxy-6,6-diphenylcyclotriphosphazatriene (XII).—2,2-Diamino-4,4-dichloro-6,6-diphenylcyclotriphosphazatriene (5.0 g, 0.0128 mole; mp 161–165°) was treated with sodium phenoxide (0.050 mole) in boiling acetone (200 ml) for 24 hr, and XII, mp 145–151°, was obtained in 71% yield (4.6 g, 0.091 mole). Recrystallization from ethanol gave a pure sample (3.8 g), mp 150–152°.

2,2,4,4-Tetraphenoxy-6,6-diphenylcyclotriphosphazatriene.—2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene (5.00 g, 0.0116 mole) was treated with sodium phenoxide (0.051 mole) in boiling acetone (280 ml) for 24 hr, and crude 2,2,4,4-tetraphenoxy-6,6-diphenylcyclotriphosphazatriene, mp 79.5–81.5°, was obtained in 79% yield (6.09 g, 0.0082 mole). Recrystallization from ethanol gave a sample, mp 97–98°.

Anal. Calcd for $P_3N_3(C_6H_5)_2(OC_6H_5)_4$: C, 65.36; H, 4.57; N, 6.35. Found: C, 65.16; H, 4.72; N, 6.61.

Check of Absence of Isomerization during Phenoxylation.—A solution of *cis*-2,4-dichloro-2,4,6,6-tetraphenoxycyclotriphosphazatriene (II) (5.00 g, 0.00865 mole; mp 74–76°) and sodium phenoxide (0.0030 mole) in acetone (200 ml) was stirred for 24 hr at room temperature and then evaporated. To the residue ether and water were added; the ether layer was separated and the aqueous layer extracted once with ether. The combined ether solution was dried ($CaCl_2$) and evaporated leaving an oil (6.97 g), which contained acetone. The oil was dissolved in ether (80 ml), and the solution was left standing with liquid ammonia (*ca.* 100 ml) in an autoclave for 96 hr. The resulting mixture was filtered, the filtrate was evaporated, and the remaining oil (5.97 g) was chromatographed on acid-washed alumina (150 g). Aminopentaphenoxycyclotriphosphazatriene (III), mp 65–67°, and then *cis*-2,4-diamino-2,4,6,6-tetraphenoxycyclotriphosphazatriene (VI), mp 117–119°, were eluted, but no *trans*-2,4-diamino-2,4,6,6-tetraphenoxycyclotriphosphazatriene (V) was found in the 38 chromatographic fractions. On the basis of the totals of the corresponding chromatographic fractions, the yields of III and VI were 1.61 g (0.00261 mole, 30%) and 2.97 g (0.00551 mole, 64%), respectively.

CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT,
U. S. NAVAL PROPELLANT PLANT, INDIAN HEAD, MARYLAND

Synthesis and Characterization of Some Perfluorophenylphosphine Derivatives[1,2]

BY D. D. MAGNELLI, G. TESI, J. U. LOWE, JR., AND W. E. McQUISTION

Received September 13, 1965

Bis(pentafluorophenyl)chlorophosphine and pentafluorophenyldichlorophosphine are prepared in good yields from pentafluorophenylmagnesium bromide and phosphorus trichloride. The reactions of the halophosphines with the Lewis bases water, ammonia, dimethylamine, and 2-methylaziridine produced substituted phosphines. Oxidative chlorination of bis(pentafluorophenyl)phosphinamide followed by dehydrohalogenation gave perfluorophenylphosphonitriles. The infrared and pertinent proton magnetic resonance spectra of these compounds are discussed.

Introduction

A synthetic approach similar to that used by Wall and co-workers[3] was employed in the preparation of bis(pentafluorophenyl)chlorophosphine (I) and pentafluorophenyldichlorophosphine (II) from pentafluorophenylmagnesium bromide[4] and phosphorus trichloride in stoichiometric amounts.

$$2C_6F_5MgBr + PCl_3 \longrightarrow \underset{\text{I}}{(C_6F_5)_2PCl} + 2Mg(Br)Cl$$

$$C_6F_5MgBr + PCl_3 \longrightarrow \underset{\text{II}}{C_6F_5PCl_2} + Mg(Br)Cl$$

(1) This work was supported by the Foundational Research Program of the Bureau of Naval Weapons.

(2) (a) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964; (b) presented in part at the 3rd International Fluorine Chemistry Symposium, Munich, Germany, Aug 1965.

(3) L. A. Wall, R. E. Donadio, and W. T. Pummer, *J. Am. Chem. Soc.*, **82**, 4846 (1960).

(4) E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959).