750. *Phosphorus–Nitrogen Compounds. Part XI.*[1] *Kinetic Investigations of the Reactions of Chlorocyclophosphazenes with Piperidine and Diethylamine in Toluene*

By B. Capon, K. Hills, and R. A. Shaw

The reaction of $N_3P_3Cl_6$ with piperidine in toluene at 0°c has been studied kinetically and was shown to follow a mixed second and third order rate law, and to be catalysed by tri-n-butylamine. The mechanistic implications of this are discussed. Less detailed kinetic studies were made on the following reactions in toluene: $N_3P_3Cl_5{\cdot}NC_5H_{10}$, $N_3P_3Cl_4(NC_5H_{10})_2$ (m. p. 105°), geminal $N_3P_3Ph_2Cl_4$, $N_3P_3Ph_2Cl_3{\cdot}NC_5H_{10}$, $N_3P_3Ph_2Cl_2(NC_5H_{10})_2$ (m. p. 146°), and $N_4P_4Cl_8$ with piperidine, and $N_3P_3Cl_6$, $N_3P_3Cl_5{\cdot}NEt_2$, and $N_4P_4Cl_8$ with diethylamine.

REPLACEMENT of successive chlorine atoms in hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, by a single nucleophilic reagent may lead in theory to one mono-, three di-, three tri-, three tetra-, one penta-, and one hexa-substituted derivatives, optical and conformational isomers being excluded.[2] As structural investigations of partially substituted phosphazenes were in their infancy when our kinetic studies were carried out, the investigations reported here represent merely a preliminary survey of some of the reactions of chlorocyclophosphazenes with piperidine and with diethylamine. However, as the replacement of the first chlorine atom can yield only one possible product, and since replacement of a second chlorine atom was found to be relatively slow, the kinetics of the displacement of the first chlorine atom of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, by piperidine were investigated in some detail. A preliminary account of this work has appeared.[3]

Since these kinetic studies were completed, the reaction of hexachlorocyclotriphosphazatriene with piperidine[4] in benzene has been investigated in considerable detail, and structural assignments have been made. These reveal that the mono- gives two di- (*cis* and *trans* nongeminal) derivatives, and that the 2,2,4,6-tetrachloro-4,6-dipiperidino-derivative, $N_3P_3Cl_4(NC_5H_{10})_2$, used in the present study, probably has a *trans* configuration,[4] and gives the geminal and the *trans* nongeminal tripiperidino-derivatives, $N_3P_3Cl_3(NC_5H_{10})_3$.

Kinetic measurements of the reactions of halogenocyclophosphazenes [$(NPX_2)_n$, $n = 3$ or 4, X = F, Cl, or Br] with n-butylamine in acetonitrile have been reported.[5] Considerable variations in reaction orders and rate constants were observed, and the absence of product

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[1] Part X, R. Keat, R. A. Shaw, and C. Stratton, *J.*, 1965, 2223.
[2] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.
[3] B. Capon, K. Hills, and R. A. Shaw, *Proc. Chem. Soc.*, 1962, 390.
[4] R. Keat and R. A. Shaw, unpublished results.
[5] T. Moeller and S. G. Kokalis, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1397.

analysis and of any information on whether the next replacement step is competitive allows only an overall sequence of reactivities to be deduced.

EXPERIMENTAL

Materials.—Commercial hexachlorocyclotriphosphazatriene was recrystallised from light petroleum, sublimed twice (60°/0·1 mm.), and recrystallised twice more from light petroleum, after which it had m. p. 113°. Commercial octachlorocyclotetraphosphazatetraene was recrystallised from light petroleum, sublimed (80°/0·1 mm.), and then crystallised from light petroleum to give m. p. 123—124°. Light petroleum was of b. p. 60—80°, unless otherwise stated.

Pentachloropiperidinocyclotriphosphazatriene was prepared by slowly adding piperidine (10·0 g., 0·116 mole) in ether (100 ml.) to a vigorously stirred solution of hexachlorocyclotriphosphazatriene (20·1 g., 0·058 mole) in ether (350 ml.) at −80°. The mixture was kept at −80° for 6 hr. and then allowed to warm slowly. Piperidine hydrochloride (7·1 g., 100%) was filtered off, and the filtrate was washed with dilute nitric acid, sodium hydrogen carbonate solution, and water, and dried (Na_2SO_4). After evaporation of the ether an oil remained, which was crystallised from light petroleum (b. p. 40—60°) at 0°. Four recrystallisations from light petroleum gave the pure compound, m. p. 68° (lit.,[6] 68°) (8·1 g., 36%) (Found: C, 15·3; H, 2·0; Cl, 44·9; N, 14·6. Calc. for $C_5H_{10}Cl_5N_4P_3$: C, 15·2; H, 2·0; Cl, 44·7; N, 14·1%).-2,2,4,6-Tetrachloro-4,6-dipiperidinocyclotriphosphazatriene was prepared similarly from piperidine (20 g., 0·23 mole) and hexachlorocyclotriphosphazatriene (19·6 g., 0·056 mole) in ether (400 ml.) except that the reaction mixture was left at room temperature for 2 days before the piperidine hydrochloride was separated. The product was recrystallised from light petroleum; it had m. p. 104—105° (lit.,[6] 104—105°) (8·9 g., 35%) (Found: C, 26·7; H, 4·3; Cl, 31·3; N, 16·1. Calc. for $C_{10}H_{20}Cl_4N_5P_3$: C, 27·0; H, 4·5; Cl, 31·8; N, 15·7%).

The other compounds were prepared and purified by published procedures.[7,8]

AnalaR toluene was dried over sodium wire and distilled from sodium as required to yield a product which contained 10 p.p.m. of water (Karl Fischer titration). Piperidine was dried over potassium hydroxide and distilled twice from sodium through a column (50 × 2·5 cm.) packed with glass helices. The fraction boiling at 106° was collected and had a water content of 25 p.p.m. Diethylamine was dried over potassium hydroxide and distilled twice (b. p. 55·5°), as required, from barium oxide. Its water content was 25 p.p.m.

Triethylamine was boiled under reflux for 8 hr. with acetic anhydride to remove primary and secondary amines. The tertiary base was then distilled from the mixture, dried over potassium hydroxide, and distilled (b. p. 89·5°) four times from phosphorus pentoxide; it then had a water content >500 p.p.m. Further distillations from barium oxide did not reduce this value to below 400 p.p.m.

Tri-n-butylamine was boiled under reflux for 12 hr. with acetic anhydride. The product was distilled at atmospheric pressure to yield first unchanged acetic anhydride and then tri-n-butylamine. This was dried first over potassium hydroxide, then over sodium wire and redistilled, b. p. 214—216°. It had a water content of <50 p.p.m., but was very hygroscopic and was redistilled before use.

Kinetic Measurements.—Reactions at 0·0° ± 0·05° were carried out in a Dewar vessel (4 l. capacity) filled with an ice–water mixture which was stirred manually at intervals. A conventional thermostat was used for reactions at 25·0° ± 0·05°. Since piperidine hydrochloride is precipitated during the reaction, it was necessary to use the method of separate bulbs. With the slower reactions, for which the temperature was 25° and the concentration of chlorophosphazene 0·0500M, ground-stoppered tubes (12 × 2 cm.) were used. A portion (5 ml.) of a stock solution (0·100M) of chlorophosphazene in toluene was placed in a tube and allowed to attain thermostat temperature. A portion (5 ml.) of the amine stock solution in toluene, also at 25°, was then added and after a measured time interval the reaction mixture was quenched and

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[6] A. A. Kropacheva, L. E. Mukhina, N. M. Kashnikova, and V. A. Parshina, *Zhur. obshchei. Khim.*, 1961, **31**, 1036.

[7] S. K. Ray and R. A. Shaw, *J.*, 1961, 872; K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J.*, 1964, 121.

[8] K. Hills and R. A. Shaw, *J.*, 1964, 130.

analysed as described below. The faster reactions were carried out at 0° and at higher dilutions. Chloro-compound stock solution (0·100M; 5 ml.) and additional toluene were pipetted into a 250-ml. ground-stoppered flask and allowed to equilibrate for 1 hr. in the ice–water bath. Some of the amine stock solution (at 0°) was then added and after a measured time interval the reaction mixture was quenched and analysed. Each kinetic run consisted of 8—10 such experiments, covering from 10 to 70% of the reaction, as well as an infinity observation made after about 20 half-lives.

The reactions were quenched with an excess of 6N-nitric acid. When test tubes were used, the reaction mixture and nitric acid were washed into a 250-ml. reagent bottle and chloride ion was determined by Volhard's method. With the 250-ml. flasks, the chloride was determined *in situ*.

Control experiments showed (i) that the toluene had no effect on the chloride determination, (ii) that none of the chloride of hexachlorocyclotriphosphazatriene or of octachlorocyclotetraphosphazatetraene was titrated under these conditions either in the presence or absence of piperidine, and (iii) that neither the chloro-compounds nor piperidine had any effect on the chloride determination. It was, however, found that diethylamine hindered the coagulation of the silver chloride, and that for consistent results it was necessary to leave the precipitated silver chloride for 12 hr. before titrating with ammonium thiocyanate.

Some difficulty was experienced in controlling the temperature of the faster reactions owing to the large heat of reaction. For instance, on mixing 5 ml. of a 0·200M-piperidine solution with 5 ml. of a 0·100M-hexachlorocyclotriphosphazatriene solution, both at 0°, the temperature rose to +2·8° and did not return to 0° until after 8 min. in the ice–water bath, by which time 60% reaction had occurred. This difficulty was overcome by working at a sixfold greater dilution, as the temperature rise was then negligible.

RESULTS

The Reaction of Hexachlorocyclotriphosphazatriene with Piperidine at 0°.—The isolation of an 87% yield of pentachloropiperidinocyclotriphosphazatriene, $N_3P_3Cl_5{\cdot}NC_5H_{10}$, from this reaction under the conditions of the kinetic experiments, and the observation (see below) that the pentachloro-compound reacts 40—50 times slower than hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, show that there is no significant interference from the replacement of a second chlorine atom. The reaction being studied is therefore:

$$N_3P_3Cl_6 + 2NHC_5H_{10} \longrightarrow N_3P_3Cl_5{\cdot}NC_5H_{10} + NHC_5H_{10},HCl$$

Reactions were carried out at three different initial piperidine concentrations, and rate coefficients were calculated from the integrated rate expressions derived from the equations

$$d[Cl^-]/dt = k_2'[N_3P_3Cl_6][NHC_5H_{10}]$$

$$d[Cl^-]/dt = k_{2\cdot5}'[N_3P_3Cl_6][NHC_5H_{10}]^{1\cdot5}$$

$$d[Cl^-]/dt = k_3'[N_3P_3Cl_6][NHC_5H_{10}]^2.$$

As shown in Table 1 the values of k_2' and $k_{2\cdot5}'$ decreased with increasing percentage reaction, whilst those of k_3' increased. The values of the coefficients extrapolated to zero time also varied with the initial amine concentration. This behaviour is similar to that observed by Ross and his co-workers [9] for the aminolysis of 1-chloro-2,4-dinitrobenzene and hence our results were calculated by using their equation. This, for our reaction, is

$$d[Cl^-]/dt = k_2[N_3P_3Cl_6][NHC_5H_{10}] + k_3[N_3P_3Cl_6][NHC_5H_{10}]^2 \qquad (1)$$

which on rearrangement gives

$$\frac{d[Cl^-]/dt}{[N_3P_3Cl_6][NHC_5H_{10}]} = k_2 + k_3[NHC_5H_{10}] \qquad (2)$$

The $d[Cl^-]/dt$ terms were obtained by drawing tangents on large-scale plots of % reaction against time. A reasonably good straight line could be drawn through the points obtained by plotting the left hand side of equation (2) against $[NHC_5H_{10}]$, using the method of least squares

[9] S. D. Ross, *Progr. Phys. Org. Chem.*, 1964, **1**, 55.

TABLE 1

Reaction of $N_3P_3Cl_6$ with NHC_5H_{10} in toluene at 0·0°

				∞-titration	Calc. ∞-value assuming complete reaction
$[N_3P_3Cl_6]_{t=0} = 8{\cdot}5 \times 10^{-3}$M		$[NHC_5H_{10}]_{t=0} = 8{\cdot}6 \times 10^{-3}$M			
% Chloride ion liberated * at first observn.	7·43,	at last observn.†	39·0	50·4	50·6
Calc. $10^2k_2'$ at first observn.	1·64	at last observn.†	0·81		
Calc. k_3' ,, ,,	2·02	,, ,,	2·27		
$[N_3P_3Cl_6]_{t=0} = 8{\cdot}5 \times 10^{-3}$M		$[NHC_5H_{10}]_{t=0} = 12{\cdot}9 \times 10^{-3}$M			
% Chloride ion liberated * at first observn.	14·6	at last observn.†	59·0	75·4	75·7
Calc. $10^2k_2'$ at first observn.	2·05	at last observn.†	1·03		
Calc. k_3' ,, ,,	1·82	,, ,,	2·06		
$[N_3P_3Cl_6]_{t=0} = 8{\cdot}5 \times 10^{-3}$M		$[NHC_5H_{10}]_{t=0} = 17{\cdot}2 \times 10^{-3}$M			
% Chloride ion liberated * at first observn.	22·5	at last observn.†	82·8	100·5	100·0
Calc. $10^2k_2'$ at first observn.	2·81	at last observn.†	1·26		
Calc. $10k_{2\cdot5}'$,, ,,	2·50	,, ,,	2·01		
Calc. k_3' ,, ,,	1·83	,, ,,	2·41		

* Based on initial concn. of phosphazene assuming replacement of one chlorine atom. † Prior to infinity observn.

(see Figure 1). The rate constants $k_2 = 2{\cdot}2 \times 10^{-3}$ ($\pm 7\%$) l. mole^{-1} sec.$^{-1}$ and $k_3 = 1{\cdot}7$ ($\pm 7\%$) l.^{2} mole^{-2} sec.$^{-1}$ were calculated from the intercept and slope, respectively. The variation of rate with phosphazene concentration was not determined, but in view of earlier work it seems extremely unlikely that this would be other than first order.[10]

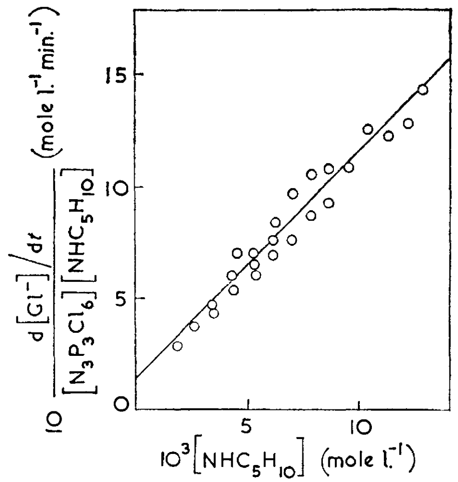

FIGURE 1. Reaction of $N_3P_3Cl_6$ with NHC_5H_{10} at 0°

Since it seemed likely (see p. 4064) that the third order term of equation (1) represents base catalysis by piperidine, the possibility of catalysis by other amines was investigated. Triethylamine could not be dried sufficiently (see p. 4060) and there was always some formation of titratable chloride in toluene solutions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, and triethylamine, due presumably to a base-catalysed hydrolysis. It was, however, possible to obtain samples of tri-n-butylamine which did not react significantly with this phosphazene. The expected rate equation in the presence of tri-n-butylamine is then

$$d[Cl^-]/dt = k_2[N_3P_3Cl_6][NHC_5H_{10}] + k_3[N_3P_3Cl_6][NHC_5H_{10}]^2 + k_3{}^*[N_3P_3Cl_6][NHC_5H_{10}][NBu^n{}_3]. \quad (3)$$

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[10] J. F. Bunnett and R. F. Zahler, *Chem. Rev.*, 1954, **49**, 273; N. B. Chapman and R. E. Parker, *J.*, 1951, 3302; R. R. Bishop, E. A. S. Cavell, and N. B. Chapman, *J.*, 1952, 437; E. A. S. Cavell and N. B. Chapman, *J.*, 1953, 3392; N. B. Chapman, R. E. Parker, and P. W. Soanes, *J.*, 1954, 2109.

In the course of the reaction, both amines are precipitated as their hydrochlorides and the concentrations of each are not known. Reactions were carried out with constant initial concentrations of the chloro-compound and piperidine, but with varying initial concentrations of tri-n-butylamine. (See Figure 2.) At zero reaction time equation (3) then becomes:

$$d[Cl^-]_0/dt_0 = k + k_3{}^*k^*[NBu^n{}_3]$$

where $k^* = [N_3P_3Cl_6]_0[NHC_5H_{10}]_0$, and $k = k^*\{k_2 + k_3[NHC_5H_{10}]_0\}$.

The rates at zero time, $d[Cl^-]_0/dt_0$, were measured by extrapolation for each concentration of tri-n-butylamine. A plot of $d[Cl^-]_0/dt_0$ against $[NBu^n{}_3]_0$ gave a good straight line (Figure 3) and $k_3{}^*$ was calculated from the slope as $1{\cdot}4 \times 10^{-2} \pm 5\%$ l.^{2} mole^{-2} sec.$^{-1}$ at 0°.

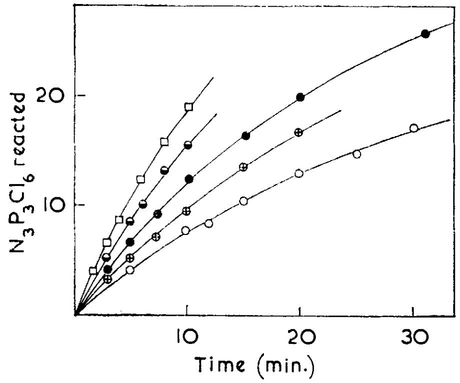

FIGURE 2. Reaction of $N_3P_3Cl_6$ ($8{\cdot}5 \times 10^{-3}$M) with NHC_5H_{10} ($8{\cdot}6 \times 10^{-3}$M) in the presence of $NBu^n{}_3$ at 0°

Initial concentration of $NBu^n{}_3$: □ 0·172M; ◒ 0·129M; ● 0·086M; ⊕ 0·043M; ○ 0·00M

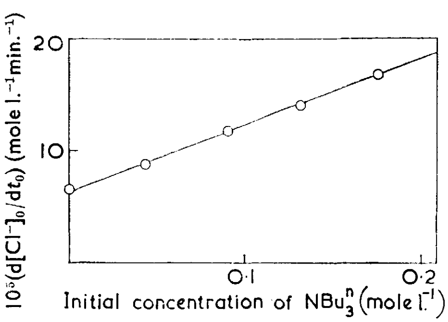

FIGURE 3. Initial rate of reaction of $N_3P_3Cl_6$ ($8{\cdot}5 \times 10^{-3}$M) with NHC_5H_{10} ($8{\cdot}6 \times 10^{-3}$M) plotted against concentration of $NBu^n{}_3$

The Reactions of Derivatives of Hexachlorocyclotriphosphazatriene with Piperidine.—These reactions were investigated in considerably less detail. The reaction of pentachloropiperidinocyclotriphosphazatriene, $N_3P_3Cl_5{\cdot}NC_5H_{10}$ (0·0165M) with piperidine (0·0330M) in toluene at 0° gave second-order rate coefficients which decreased, and third-order rate coefficients which increased with increasing percentage reaction (see Table 2). The results were, however, in good agreement with a rate equation of type (1) and constants $k_2 = 8{\cdot}6 \times 10^{-4} \pm 10\%$ l. mole^{-1} sec.$^{-1}$ and $k_3 = 2{\cdot}4 \times 10^{-2}$ l.^{2} mole^{-2} sec.$^{-1}$ were evaluated graphically. The rate of reaction of the dipiperidino-derivative under the same conditions was considerably slower and was neglected, although no quantitative comparison was made.

The reaction of 2,2,4,6-tetrachloro-4,6-dipiperidinocyclotriphosphazatriene, $N_3P_3Cl_4(NC_5H_{10})_2$ (0·05M) with piperidine (0·10M) in toluene was studied at 25°. The second- and third-order rate coefficients both increased with increasing percentage reaction (see Table 2), differing from the previous reactions where the second-order coefficients decreased. Presumably this is due to the tripiperidino-derivatives reacting at a comparable rate.

The reactions of geminal diphenyl derivatives of hexachlorocyclotriphosphazatriene with piperidine in toluene were also studied. Although it is clear that 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazatriene, $N_3P_3Ph_2Cl_4$, reacts at a slower rate than hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, calculations of rate constants were precluded since the monopiperidino-, $N_3P_3Ph_2Cl_3{\cdot}NC_5H_{10}$, and the nongeminal dipiperidino-derivative (m. p. 146°), $N_3P_3Ph_2Cl_2(NC_5H_{10})_2$, react only a little slower than the tetrachloro-compound, $N_3P_3Ph_2Cl_4$, itself.[11] The approximate half-lives of these three compounds at 25°, initial phosphazene concentration 0·05M, and initial piperidine concentration 0·10M were: $N_3P_3Ph_2Cl_4$ (150 min.), $N_3P_3Ph_2Cl_3{\cdot}NC_5H_{10}$ (480 min.), and $N_3P_3Ph_2Cl_2(NC_5H_{10})_2$ (660 min.).

The Reaction of Hexachlorocyclotriphosphazatriene with Diethylamine.—The kinetics of this

[11] K. Hills, Ph.D. Thesis, London University, 1963.

TABLE 2

Reaction of $N_3P_3Cl_5{\cdot}NC_5H_{10}$ (0·0165M) with NHC_5H_{10} (0·0330M) in toluene at 0·0°

Time (min.)	50	100	150	240	300	360	480	600	720	960	∞
% reaction *	11·4	20·4	27·9	38·0	42·5	47·0	53·6	58·9	63·4	69·4	99·8
$10^3k_2'$ (l. mole^{-1} sec.$^{-1}$)	1·30	1·26	1·30	1·29	1·24	1·23	1·22	1·21	1·21	1·19	—
$10^2k_3'$ (l.^{2} mole^{-2} sec.$^{-1}$)	4·20	4·32	4·71	5·11	5·17	5·44	5·81	6·28	6·87	7·26	—

Reaction of $N_3P_3Cl_4(NC_5H_{10})_2$ (0·0500M) with NHC_5H_{10} (0·100M) in toluene at 25·0°

Time (min.)	30	60	90	130	180	245	300	360	420	495	610	∞
% reaction *	10·8	20·4	27·7	35·8	43·5	51·5	57·2	62·6	66·4	70·4	74·7	100·2
$10^4k_2'$ (l. mole^{-1} sec.$^{-1}$)	6·72	6·96	7·10	7·15	7·13	7·21	7·37	7·75	7·84	8·01	8·07	—
$10^2k_3'$ (l.^{2} mole^{-2} sec.$^{-1}$)	7·15	8·03	8·45	8·85	9·88	11·1	12·4	14·2	15·6	17·5	20·0	—

Reaction of $N_3P_3Cl_6$ (5·00 × 10^{-2}M) with $NHEt_2$ (1·00 × 10^{-1}M) in toluene at 25·0°

Time (min.)	10	20	30	60	90	120	180	240	300	360	420	480	600	∞
% reaction *	5·7	9·3	13·4	20·4	27·6	33·1	41·8	47·5	52·6	56·5	60·6	63·1	67·7	100·2
$10^4k_2'$ (l. mole^{-1} sec.$^{-1}$)	10·08	8·54	8·60	7·12	7·06	6·87	6·66	6·28	6·16	6·16	6·10	5·93	5·82	—
$10^2k_3'$ (l.^{2} mole^{-2} sec.$^{-1}$)	1·04	0·90	0·92	0·80	0·84	0·92	0·88	0·91	0·96	0·99	1·08	1·10	1·19	—

Reaction of $N_3P_3Cl_5{\cdot}NEt_2$ (5·00 × 10^{-2}M) with $NHEt_2$ (1·00 × 10^{-1}M) in toluene at 25·0°

Time (hr.)	3·5	17
% reaction *	2·5	10·5

Reaction of $N_4P_4Cl_8$ (8·50 × 10^{-3}M) with $NHEt_2$ (17·2 × 10^{-3}M) in toluene at 0·0°

Time (min.)	5	10	15	22·5	30	45	60	∞
% reaction *	15·0	27·4	35·0	43·1	49·9	58·9	66·0	100·3
$10^2k_2'$ (l. mole^{-1} sec.$^{-1}$)	3·50	3·65	3·47	3·10	3·20	3·06	3·10	—
$10k_3'$ (l.^{2} mole^{-2} sec.$^{-1}$)	2·17	2·50	2·61	2·63	2·78	2·96	3·48	—

* Assuming one chlorine atom is displaced from each molecule of chloro-compound.

reaction (see Table 2) were similar to those observed for the reaction with piperidine, and the results were calculated similarly; at 25°, $k_2 = 4.4 \times 10^{-4} \pm 5\%$ l. mole^{-1} sec.$^{-1}$, $k_3 = 2.9 \times 10^{-3} \pm 5\%$ l.^{2} mole^{-2} sec.$^{-1}$.

The Reactions of Octachlorocyclotetraphosphazatetraene.—The reaction between octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$ (8·50 × 10^{-3}M), and piperidine (1·72 × 10^{-2}M) in toluene at 0° was too fast to be followed by the present technique. In 10 min. there was over 90% reaction. Under the same conditions the reaction with diethylamine was fast but measurable (see Table 2). The possibility of competition from the reaction of heptachlorodiethylaminocyclotetraphosphazatetraene, $N_4P_4Cl_7{\cdot}NEt_2$, could not be examined, since this compound had not been prepared. However, it is probable that its reactivity is considerably less than that of the octachloro-compound, $N_4P_4Cl_8$, since the second-order rate coefficients for the reaction of the latter compound with diethylamine decreased with increasing percentage reaction, but the results were not analysed further.

DISCUSSION

The reactions of hexachlorocyclotriphosphazatriene in toluene with piperidine and diethylamine obey the following rate expression:

$$d[\text{product}]/dt = k_2[\text{chloro-compound}][\text{amine}] + k_3[\text{chloro-compound}][\text{amine}]^2$$

and the reaction with piperidine was shown to be catalysed by tri-n-butylamine. This behaviour is similar to that observed for the reaction of 1-chloro-2,4-dinitrobenzene with aliphatic amines in chloroform,[9] but the third-order term observed in the present study is relatively more important than those observed in the benzenoid system. Base catalysis has also been observed in the reaction of 1-fluoro-2,4-dinitrobenzene with *N*-methylaniline in ethanol and in aqueous dioxan. Bunnett [12] has argued convincingly that this provides

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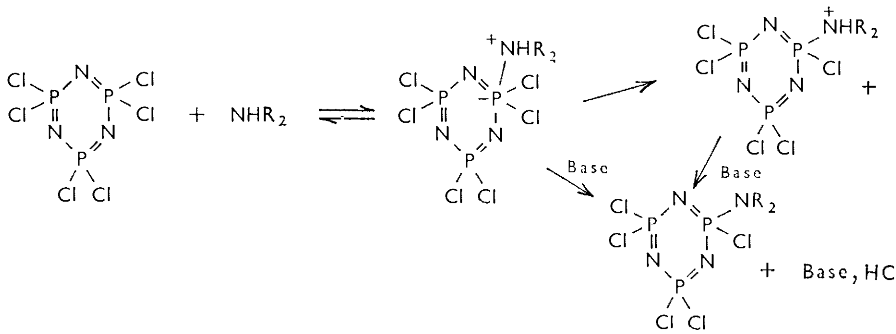
[12] J. F. Bunnett and J. T. Randall, *J. Amer. Chem. Soc.*, 1958, **80**, 6020.

good evidence for a tetrahedral intermediate, the base catalysis being associated with the removal of a proton from this intermediate either before, or synchronous with, the expulsion of a chloride ion. An analogous mechanism may be written for the reaction of hexachlorocyclotriphosphazatriene involving a pentaco-ordinated intermediate, as shown in the scheme, and the intervention of a base-catalysed dehydrochlorination step in the hydrolysis of a structurally related phosphorochloramidate is well established.[13]



(In view of the structural complexity of the phosphazenes the precise electronic structure of the intermediate is uncertain)

It is, however, less certain whether the observation of a third-order term in the rate law of reactions with amines in aprotic solvents requires such an interpretation. Presumably in these solvents there will be extensive complex formation through hydrogen bonding between amine molecules, and the varying kinetic order may merely reflect the varying degree of polymerisation of the amine with concentration. This explanation is similar to that offered by several workers for the varying kinetic order observed for reactions of certain chloro-compounds with ethanol and with water in aprotic solvents.[14]

The rate of reaction of hexachlorocyclotriphosphazatriene with piperidine is about 50 times greater than that of its monopiperidino-derivative, $N_3P_3Cl_5{\cdot}NC_5H_{10}$, and about 500 times greater than that of its dipiperidino-derivative, $N_3P_3Cl_4(NC_5H_{10})_2$. As a working hypothesis it will be assumed that the third-order term in the rate expression arises from a base-catalysed dehydrochlorination of a pentacovalent intermediate, but the above reservation should be borne in mind. Since a nongeminal chlorine atom is replaced in the first two of these reactions, the large substituent effect suggests that charge is delocalised at least partly into the ring in the transition state. The third-order term in the rate expression is relatively less important in the reaction of the monopiperidino derivative than that of the hexachloro-compound. This is not unreasonable on the intermediate-complex hypothesis, as the electron release by the piperidino-substituent already present will favour the expulsion of the chloride ion, and thus increase the ratio of the second-order to third-order term relative to that for the hexachloro-compound, $N_3P_3Cl_6$.

The rate of reaction of hexachlorocyclotriphosphazatriene with piperidine is about 10^3 times faster than that with diethylamine, although in water and in nitrobenzene these amines are of comparable basicity.[15,16] This rate difference is similar to that observed by Brady

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[13] E. W. Crunden and R. F. Hudson, *Chem. and Ind.*, 1958, 1478; *J.*, 1962, 3591; F. H. Westheimer, *Chem. Soc. Spec. Publ.*, 1957, **8**, 181; R. F. Hudson in " Advances in Inorganic Chemistry and Radiochemistry," ed. H. J. Emeléus and A. G. Sharpe, Academic Press Inc., New York, 1963, vol. V, p. 347; Symposium on Organophosphorus Compounds, Heidelberg, 1964.

[14] R. F. Hudson and B. Saville, *J.*, 1955, 4114, 4121, 4136; R. F. Hudson and I. Steltzer, *Trans. Faraday Soc.*, 1958, **54**, 213; J. R. Chipperfield and R. H. Prince, *J.*, 1963, 3567; R. F. Hudson, *Ber. d. Bunsengesellschaft f. Phys. Chem.*, 1964, **68**, 215.

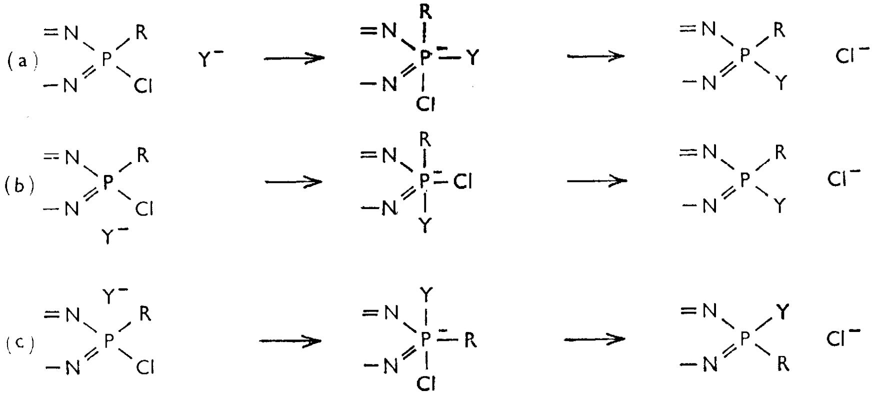
[15] D. Feakins, W. A. Last, and R. A. Shaw, *J.*, 1964, 2387.

[16] H. K. Hall, *J. Phys. Chem.*, 1956, **60**, 63.

and Cropper[17] for the reactions of 1-chloro-2,4-dinitrobenzene with these amines and may be explained similarly as being due to the greater steric requirements of diethylamine. The reduced importance of the third-order term in the reaction with diethylamine presumably also arises from steric factors.

Octachlorocyclotetraphosphazatetraene reacts 10^2—10^3 times more rapidly than hexachlorocyclotriphosphazatriene with diethylamine. An explanation for this is not easy to see, cf. refs. 5 and 18. Possibly the eight-membered ring accommodates the negative charge in the transition state more readily than the six-membered one.

The stereochemical course of replacement reactions of phosphazenes is unknown. Reaction may occur with attack by the amine in the plane of the ring, as suggested by Bailey and Parker,[19] or perpendicular to the ring. With planar attack (a) retention of configuration must occur, but with perpendicular attack retention or inversion is possible, depending on whether the approach of the amine is from below (b) or from above the ring (c). Substitution at tetra-co-ordinated phosphorus has been shown to occur in some circumstances with inversion of configuration (see ref. 20). Whilst in the system which we have investigated the phosphorus atoms are part of a ring, which may impose additional steric constraints, the observation that amine hydrochlorides cause *cis-trans* isomerisation of nongeminal aminochlorocyclotriphosphazatrienes[21] makes us favour the reaction course depicted in (c).



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[17] O. L. Brady and F. R. Cropper, *J.*, 1950, 507.
[18] N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168.
[19] J. V. Bailey and R. E. Parker, *Chem. and Ind.*, 1962, 1823.
[20] M. Green and R. F. Hudson, *Proc. Chem. Soc.*, 1962, 307; *J.*, 1963, 540.
[21] R. Keat and R. A. Shaw, *Chem. and Ind.*, 1964, 1232; *J.*, following Paper.