Studies of Phosphazenes. Part 31.[1] Kinetic Studies of the Reactions of Hexachlorocyclotriphosphazene with Aromatic Primary Amines: Evidence for the Intermediacy of a Reactive Three-co-ordinated Phosphorus(v) Species

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Kinetic studies of the reactions of hexachlorocyclotriphosphazene with aromatic primary amines (aniline, *p*-toluidine, and *p*-anisidine) have been investigated with a view to developing 'model systems' for analogous reactions with aromatic diamines. The first and second stages of chlorine replacement proceed by an $S_N2(P)$ mechanism in both tetrahydrofuran (thf) and methyl cyanide. Kinetic evidence is obtained for a base-catalysed E_1(c.b.) mechanism for the formation of geminal products in thf in the presence of an excess of tri-n-butylamine. The intermediacy of a three-co-ordinate P^V species is established by trapping experiments with methanol and by the isolation of the unusual products $[NHEt_3][gem\text{-}N_3P_3Cl_4(NHR)(O)]$ [R = Ph, C_6H_4Me-*p*, or $C_6H_4(OMe)$-*p*]. These triethylammonium salts on dimethylaminolysis afford the hydroxy derivatives *gem*-$N_3P_3(NHR)(OH)(NMe_2)_4$, which exist in their oxophosphazadiene tautomeric forms.

The products of the reactions of $N_3P_3Cl_6$ with aromatic primary amines under various experimental conditions have been described in the preceding paper.[1] In this paper, the results of kinetic studies on the same systems are reported and their mechanistic implications discussed. Evidence for a three-co-ordinated P^V species, which is an intermediate in the formation of the geminal bis(primary amino)cyclotriphosphazenes, has been obtained for the first time in cyclophosphazene chemistry. This investigation is a continuation of our previous studies designed to unravel the mechanism of aminolysis reactions of halogenocyclophosphazenes.[2,3]

Experimental

Materials.—Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), was prepared and purified by a standard method.[4] The solvents were purified by conventional procedures. The purification of aniline, *p*-toluidine, and *p*-anisidine and the preparation of the mono(arylamino) derivatives, $N_3P_3Cl_5(NHR)$ [R = Ph (**2**), C_6H_4Me-*p* (**3**), or $C_6H_4(OMe)$-*p* (**4**)], were as described in the preceding paper.[1] For kinetic studies, (**3**) was further purified by column chromatography over silica gel using light petroleum (b.p. 60—80 °C) as eluant and (**4**) was recrystallized from methylene chloride–light petroleum (1:4) at 0 °C. Tri-n-butylamine (Fluka) was dried with potassium hydroxide pellets, distilled under reduced pressure (80 °C/0.1 Torr, ≈ 13 Pa), and stored over molecular sieves (4 Å).

Procedure for Kinetic Studies.—The rates of reactions (i)—(ix) were measured in the temperature range 20—40 °C by employing the 'separate bulbs' technique and estimating the amine hydrochloride by a potentiometric method.[2]

$$N_3P_3Cl_5(X) + 2NH_2R \xrightarrow{\text{solvent}} \text{non-}gem\text{-}N_3P_3Cl_4(X)(NHR) + NH_3RCl$$

X = Cl, R = Ph, solvent = MeCN (i)

X = Cl, R = C_6H_4Me-*p*, solvent = MeCN (ii)

X = Cl, R = $C_6H_4(OMe)$-*p*, solvent = MeCN (iii)

X = Cl, R = $C_6H_4(OMe)$-*p*, solvent = thf (iv)

X = NHR, R = C_6H_4Me-*p*, solvent = MeCN (v)

X = NHR, R = $C_6H_4(OMe)$-*p*, solvent = MeCN (vi)

X = NHR, R = $C_6H_4(OMe)$-*p*, solvent = thf (vii)

$$N_3P_3Cl_5(NHR) + NH_2R + NBu^n_3 \text{ (excess)} \xrightarrow{\text{thf}} gem\text{-}N_3P_3Cl_4(NHR)_2 + NHBu^n_3Cl$$

R = C_6H_4Me-*p* (viii)

R = $C_6H_4(OMe)$-*p* (ix)

In all the reactions, the hydrochloride precipitated as the reaction progressed because of its poor solubility in MeCN or tetrahydrofuran (thf). All the tubes were rinsed with 0.1 mol dm^{-3} nitric acid (5 cm^3) and this solution was added to the quenching mixture. Reactions (v)—(vii) were slow and required higher concentrations of the reactants (Table 1) in order to reduce the overall reaction time, even for following the reaction to the extent of 50%. For reactions (viii) and (ix), the tertiary amine and the reacting amine were mixed together in thf and equilibrated for 1 h before adding the phosphazene solution.

Rate constants and activation parameters were evaluated on a DEC 1090 computer using a least-squares curve fitting program and appropriate rate expressions.[5–7] The data are summarized in Table 1. The rate constants for reactions (viii) and (ix) are presented in Table 2.

Kinetic studies of further chlorine replacement reactions could not be carried out because of the complications involved in the formation of more than one product.

Characterization of Products.—The products of reactions (i)—(ix) were identified by t.l.c. and characterized by ^1H n.m.r. spectra of the corresponding methoxy derivatives.[1] The *cis* and *trans* isomer ratio was found to be 1:2 for the non-geminal compounds formed in reactions (v) and (vi) after 6 h. The isomer ratio for reaction (vii) could not be ascertained under kinetic conditions because the extent of the reaction was low (< 25%), even with high concentrations of the reactants.

Reaction of $N_3P_3Cl_5(NHC_6H_4Me$-*p*) (**3**) *with Triethylamine.*—Compound (**3**) (0.42 g, 1 mmol) was dissolved in freshly-distilled thf (50 cm^3). Triethylamine (1.4 cm^3, 10 mmol) in the same solvent (50 cm^3) was rapidly added and the mixture stirred for 6 h under a dry nitrogen atmosphere. Triethylamine

hydrochloride (80 mg) was filtered off and thf from the filtrate was evaporated under reduced pressure. The residue was extracted with benzene (25 cm^3) and filtered again. Benzene was evaporated from the filtrate to obtain $[NHEt_3][gem\text{-}N_3P_3Cl_4(NHC_6H_4Me\text{-}p)(O)]$ (**6**) (0.4 g, 80%). Similarly, $[NHEt_3][gem\text{-}N_3P_3Cl_4(NHR)(O)]$ [R = Ph (**5**) or $C_6H_4(OMe)$-*p* (**7**)] were isolated.

Reaction of (**3**) *with Triethylamine in the Presence of Methanol.*—Compound (**3**) (1.0 g, 2.4 mmol) was dissolved in thf (50 cm^3). Methanol (0.1 cm^3, 2.4 mmol) was added followed by triethylamine (3.32 cm^3, 24 mmol) in thf (25 cm^3). The reaction mixture was stirred for 24 h and the solvent evaporated. The residue was extracted with benzene (100 cm^3) and filtered through a silica gel column. Benzene from the eluate was evaporated and the residue recrystallized from light petroleum (b.p. 60—80 °C) to obtain $gem\text{-}N_3P_3Cl_4(NHC_6H_4Me\text{-}p)(OMe)$ (**12**) (0.65 g, 65.7%).

Dimethylamination of (**5**)—(**7**) *and* (**12**).—Dimethylamination of the title compounds was carried out with an excess of dimethylamine in chloroform to obtain $gem\text{-}N_3P_3(NHR)(OH)(NMe_2)_4$ [R = Ph (**8**), C_6H_4Me-*p* (**9**), or $C_6H_4(OMe)$-*p* (**10**)] and $gem\text{-}N_3P_3(NHC_6H_4Me\text{-}p)(OMe)(NMe_2)_4$ (**13**), respectively. The 'hydroxy' derivative (**9**) was treated with a 10-fold excess of triethylamine in dichloromethane to afford the triethylammonium salt, $[NHEt_3][gem\text{-}N_3P_3(NHC_6H_4Me\text{-}p)(O)(NMe_2)_4]$ (**11**) (yield 90%).

The formulae of all the new compounds were inferred from the relative integrated intensities of the various resonances observed in their ^1H n.m.r. spectra. The triethylammonium salt (**6**) and the hydroxy derivative (**9**) were characterized by C, H, and N analyses [Found for (**6**): C, 32.3; H, 4.6; N, 13.8. $C_{13}H_{20}Cl_4N_5OP_3$ requires C, 31.2; H, 4.8; N, 14.0%. Found for (**9**): C, 41.7; H, 7.7; N, 25.0. $C_{15}H_{33}N_8OP_3$ requires C, 41.5; H, 7.7; N, 25.8%]. The i.r. spectra of (**5**)—(**11**) exhibit bands at 3 150—3 450, and 1 120—1 250 cm^{-1} attributable to ν(N–H) and ν(P=N) respectively; additionally, the spectra of (**8**)—(**10**) show peaks at 2 580—2 720 cm^{-1} attributable to ν(NH) of the (P–NH–P) unit.

Phosphorus-31 n.m.r. spectroscopic data are presented in Table 3 together with selected ^1H n.m.r. data.

Table 1. Summary of kinetic results[a] obtained for reactions (i)—(vii)

Reaction	Reaction medium	k_2/dm^3 mol^{-1} s^{-1} (T/K)	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
(i)[b]	MeCN	2.09×10^{-3} (293)	29.1	−203.9
		3.25×10^{-3} (303)		
		4.79×10^{-3} (313)		
(ii)[c]	MeCN	7.58×10^{-3} (298)	32.7	−155.7
		11.65×10^{-3} (308)		
		15.13×10^{-3} (313)		
(iii)[d]	MeCN	2.67×10^{-2} (298)	25.2	−189.5
		3.76×10^{-2} (308)		
		4.60×10^{-2} (313)		
(iv)[e]	thf	1.92×10^{-3} (293)	21.9	−261.7
		2.79×10^{-3} (303)		
		3.65×10^{-3} (313)		
(v)[f]	MeCN	1.43×10^{-4} (293)	32.1	−232.2
		2.30×10^{-4} (303)		
		3.54×10^{-4} (313)		
(vi)[g]	MeCN	5.05×10^{-4} (293)	33.6	−196.3
		7.83×10^{-4} (303)		
		13.05×10^{-4} (313)		
(vii)[h]	thf	1.19×10^{-4} (303)	29.1	−278.2
		1.74×10^{-4} (313)		

[a] Error involved in each parameter is <5%. [b] $[N_3P_3Cl_6]_0 = 2.5 \times 10^{-2}$ mol dm^{-3}, $[aniline]_0 = 2.5 \times 10^{-2}$—$5.0 \times 10^{-2}$ mol dm^{-3}. [c] $[N_3P_3Cl_6]_0 = 2.5 \times 10^{-3}$—$1.13 \times 10^{-2}$ mol dm^{-3}, $[p\text{-toluidine}]_0 = 5 \times 10^{-3}$—$2 \times 10^{-2}$ mol dm^{-3}. [d] $[N_3P_3Cl_6]_0 = 5 \times 10^{-3}$ mol dm^{-3}, $[p\text{-anisidine}]_0 = 8 \times 10^{-3}$—$10 \times 10^{-3}$ mol dm^{-3}. [e] $[N_3P_3Cl_6]_0 = [p\text{-anisidine}]_0 = 1.25 \times 10^{-2}$—$2.5 \times 10^{-2}$ mol dm^{-3}. [f] $[N_3P_3Cl_5(NHC_6H_4Me\text{-}p)]_0 = 5 \times 10^{-2}$ mol dm^{-3}, $[p\text{-toluidine}]_0 = 8 \times 10^{-2}$—$10 \times 10^{-2}$ mol dm^{-3}. [g] $[N_3P_3Cl_5\{NHC_6H_4(OMe)\text{-}p\}]_0 = 4 \times 10^{-2}$ mol dm^{-3}, $[p\text{-anisidine}]_0 = 4 \times 10^{-2}$—$8 \times 10^{-2}$ mol dm^{-3}. [h] $[N_3P_3Cl_5\{NHC_6H_4(OMe)\text{-}p\}]_0 = 0.6$—0.7 mol dm^{-3}, $[p\text{-anisidine}]_0 = 0.7$—1.4 mol dm^{-3}.

Results and Discussion

The kinetic data for reactions (i)—(vii) fit into a second-order rate law, first order with respect to each of the reactants. The product of each of the reactions (v)—(vii) is the non-geminal bis(arylamino) derivative; this derivative is obtained as a mixture of *cis* and *trans* isomers. The ratio of *cis* and *trans* isomers for reactions (v) and (vi) is 1:2 under the conditions (6 h) in which the kinetic studies have been carried out. But when these reactions are prolonged (>24 h), the product consists of a mixture of *cis* and *trans* isomers in almost equal amounts. It is well known that *cis–trans* isomerization can be effected by amine hydrochlorides.[8] Therefore, when the reaction is carried out for prolonged durations, a change in the proportion of the *cis* isomer is observed as a result of the secondary isomerization step. In order to confirm this conclusion, non-$gem\text{-}N_3P_3Cl_4[NHC_6H_4(OMe)\text{-}p]_2$ of a known isomeric composition (*cis*:*trans* = 1:2)[1] was treated with *p*-anisidine hydrochloride in MeCN; analysis of the product obtained after 7 d shows that *cis* and *trans* isomers are present in almost equal amounts. The isomeric composition of the bis derivative formed in reaction (vii) could not be ascertained. Reaction (vii) is slow and has been followed only up to 20% completion. The signals arising from the methoxy protons for the *cis* and *trans* isomers in the ^1H n.m.r. spectrum (270 MHz) of the methoxylated reaction mixture are too complex to be analysed unambiguously.

The second-order rate constants for reactions (v)—(vii) thus represent the combined rate for the formation of *cis* and *trans* isomers. However, deviation from linearity in the appropriate kinetic plots for these reactions is not observed. The correlation coefficient in all cases is ≥0.98. In view of this observation, as well as the isomerization experiment discussed above, it is

Table 2. Rate constants[a] for reactions (viii) and (ix) at 30 °C

	R = C_6H_4Me-*p*						R = $C_6H_4(OMe)$-*p*					
$[NBu^n_3]_0$/mol dm^{-3}	7.5×10^{-2}[b]	15×10^{-2}[b]	22.5×10^{-2}[b]	30×10^{-2}[b]	15×10^{-2}[c]	15×10^{-2}[d]	0.1[e]	0.2[e]	0.4[e]	0.6[e]	0.8[e]	1.0[e]
$10^5 k'_1/s^{-1}$	2.53	4.50	6.55	8.96	4.49	4.08	2.52	4.76	9.19	14.03	19.32	23.47

[a] Error in the individual rate constants is <5%. [b] $[N_3P_3Cl_5(NHR)]_0 = [NH_2R]_0 = 7.5 \times 10^{-3}$ mol dm^{-3}. [c] $[N_3P_3Cl_5(NHR)]_0 = [NH_2R]_0 = 1.5 \times 10^{-2}$ mol dm^{-3}. [d] $[N_3P_3Cl_5(NHR)]_0 = 1.5 \times 10^{-2}$ mol dm^{-3}, $[NH_2R]_0 = 7.5 \times 10^{-3}$ mol dm^{-3}. [e] $[N_3P_3Cl_5(NHR)]_0 = [NH_2R]_0 = 1.0 \times 10^{-2}$ mol dm^{-3}.

Table 3. Phosphorus-31 and ^{1}H n.m.r. data for oxophosphazadienes and their salts derived from (arylamino)cyclotriphosphazenes

Compound[a]	M.p./°C	^{31}P N.m.r.[b] $\delta(P_A)$	$\delta(P_B)$ or $\delta(P_X)$	^2J(P–N–P)	^{1}H N.m.r. $\delta(NMe_2)$ or δ(OMe)	^3J(P–H)
(**5**) [$NHEt_3$][*gem*-$N_3P_3Cl_4(NHR^1)(O)$][c]	105—110	−9.6	16.7	43.9		
(**6**) [$NHEt_3$][*gem*-$N_3P_3Cl_4(NHR^2)(O)$][c]	130—140	−8.5	16.8	43.1		
(**7**) [$NHEt_3$][*gem*-$N_3P_3Cl_4(NHR^3)(O)$][c]	138	−6.5	16.9	43.4		
(**8**) *gem*-$N_3P_3(NHR^1)(OH)(NMe_2)_4$[d]	160—167	−5.0[e]	18.0[f]	31.3	2.51—2.72[g]	
(**9**) *gem*-$N_3P_3(NHR^2)(OH)(NMe_2)_4$[d]	185—195	−5.1[e]	22.5[f]	30.1	2.58—2.70[g]	
(**10**) *gem*-$N_3P_3(NHR^3)(OH)(NMe_2)_4$[d,h]	105—110				2.30—2.82[g]	
(**11**) [$NHEt_3$][*gem*-$N_3P_3(NHR^2)(O)(NMe_2)_4$]	187—202	−4.7	22.7	30.8	2.60[i]	11.5
					2.53[j]	11.0
(**12**) *gem*-$N_3P_3Cl_4(NHR^2)(OMe)$	111	5.3	16.9	54.3	3.73	13.5
(**13**) *gem*-$N_3P_3(NHR^2)(OMe)(NMe_2)_4$	126—129	19.9	30.6	49.6	2.56[i]	11.0
					2.62[i]	11.0
					3.57[j]	12.0

[a] R^1 = Ph, R^2 = C_6H_4Me-*p*, R^3 = C_6H_4(OMe)-*p*. [b] Phosphorus-31 n.m.r. spectra (32.2 MHz) of all the compounds are of the AB_2 or AX_2 spin type; chemical shifts (δ) in p.p.m. are relative to 85% H_3PO_4 with downfield shifts positive; coupling constants are in Hz. [c] $\delta(NCH_2)$ = 3.04, $\delta(CH_2CH_3)$ = 1.32 p.p.m., and ^3J(H–H) = 7.3 Hz; $\delta(N^+H)$ is observed in the range 11.5—12.5 p.p.m. [d] Exists in the oxophosphazadiene tautomeric form. [e] Average chemical shift of $P(O)(NHR)$ of the two tautomers (Figure 4) observed as a triplet at 20 °C. [f] Average chemical shift of $P(NMe_2)_2$ of the two tautomers (Figure 4) observed as a broad peak at 20 °C. [g] Broad peaks in the specified region. [h] ^{31}P Spectrum not recorded. [i] Exhibits 'virtual coupling.' [j] *OMe*.

reasonable to assume that the kinetically controlled product is the *trans* isomer[3] and that the *cis* isomer is formed only to a small extent (5—10%) by the direct displacement reaction. As the reaction time increases, the isomerization of the *trans* isomer to its *cis* counterpart proceeds at a rate comparable to the rate of formation of the *trans* isomer.

The second-order kinetics observed for reactions (i)—(vii) are in accord with a bimolecular $S_N2(P)$ mechanism. The bimolecular mechanism may involve the formation of a five-co-ordinate intermediate in a fast pre-equilibrium step followed by slow decomposition of the intermediate as the rate-determining step [Figure 1(*a*)], or it may proceed by a one-step concerted mechanism [Figure 1(*b*)]. A spectrum of rate profiles in between these two limiting cases can be envisaged.[9] Activation parameters can often provide a clue as to the nature of the mechanism that operates in a particular system.[3]

The enthalpies and entropies of activation ($\Delta H^‡$ and $\Delta S^‡$) for the reactions of chlorocyclotriphosphazenes with aniline, *p*-toluidine, and *p*-anisidine [reactions (i)—(vii)] in different solvents are listed in Table 1. The data suggest that reactions (i) and (ii) essentially involve a five-co-ordinate intermediate.[2,3] The $\Delta H^‡$ value for reaction (ii) is slightly greater than that for reaction (i). The $\Delta H^‡$ value for the analogous reaction with *p*-anisidine [reaction (iii)] is reduced by ~7 kJ mol^{-1} and this result is best explained by assuming that the reaction is concerted to some extent. A possible reason for this behaviour is that the electron-releasing character of the methoxy group in *p*-anisidine increases the negative charge on the nitrogen atom which would in turn favour a concerted type of mechanism. The $\Delta S^‡$ values are also in accord with the above interpretation. The activation parameters for the reaction of $N_3P_3Cl_6$ with *p*-anisidine in thf [reaction (iv)] are consistent with the involvement of a five-co-ordinate intermediate.[3]

The $\Delta H^‡$ values for reactions (ii) and (v) are almost the same but $\Delta S^‡$ decreases by 77 J K^{-1} mol^{-1} for reaction (v) compared to reaction (ii). This decrease implies that reaction (v) involves a highly polar transition state such as that envisaged in an $S_N2(P)$ concerted mechanism.[3,10]

The $\Delta H^‡$ value for the second stage of chlorine replacement with *p*-anisidine in MeCN [reaction (vi)] is higher (8.4 kJ mol^{-1}) compared to the first chlorine replacement with the same nucleophile in the same solvent [reaction (iii)]. This trend indicates that reaction (vi) occurs by an $S_N2(P)$ mechanism involving a five-co-ordinate intermediate. It has been pointed out earlier that the first stage of chlorine replacement by *p*-anisidine in MeCN [reaction (iii)] is concerted to some degree (see above). The apparent anomaly can be explained on the basis of the basicity of the ring nitrogen atom. The presence of the *p*-anisidino group on the phosphazene ring [substrate (**4**)] increases the basicity of the ring nitrogen atoms adjacent to the phosphorus atom containing this group. The attack takes place at the $\equiv PCl_2$ centre. The five-co-ordinate intermediate formed [(**A**) in Figure 2] can be stabilised because of the high basicity of the ring nitrogen between the two phosphorus atoms bearing the amino groups and hence the $S_N2(P)$ mechanism involving a five-co-ordinate intermediate is favoured for reaction (vi).

The $\Delta H^‡$ value for the reaction of (**4**) with *p*-anisidine in thf [reaction (vii)] is higher (7.2 kJ mol^{-1}) compared to the first chlorine replacement [reaction (iv)] in the same solvent. This increase indicates that reaction (vii) occurs by an $S_N2(P)$ mechanism involving a five-co-ordinate intermediate. The $\Delta S^‡$ values for the reactions (iv) and (vii) which are similar support the proposed involvement of a five-co-ordinate intermediate.

The second-order rate constants for the reaction of $N_3P_3Cl_6$ with dimethylamine in thf[11] and methyl cyanide[3] show that the reaction is ~10 times faster in methyl cyanide. A similar trend is observed when the rate constants for the reaction of $N_3P_3Cl_6$ with *p*-anisidine in the two solvents are compared (Table 1). The reactivity of *p*-anisidine towards $N_3P_3Cl_6$ is ~5 000 times slower than that of dimethylamine. In general the activation parameters correlate with the interpretation discussed above. An amination reaction in thf essentially involves the intermediacy of a five-co-ordinated phosphorus species whereas in methyl cyanide the reaction is more likely to lean towards the one-step concerted mechanism (Figure 1).

The kinetic data for reactions (viii) and (ix) follow a pseudo-first-order rate law. The rates of these reactions are independent of the concentration of the aromatic primary amine but dependent on the cyclophosphazene concentration. If the pseudo-first-order rate constants are plotted against the initial concentration of tri-n-butylamine, a straight line is obtained with a correlation coefficient of 0.99 for both reactions (viii) and (ix). This result shows that the reaction proceeds by an E_1(c.b.) mechanism involving the formation of a reactive three-

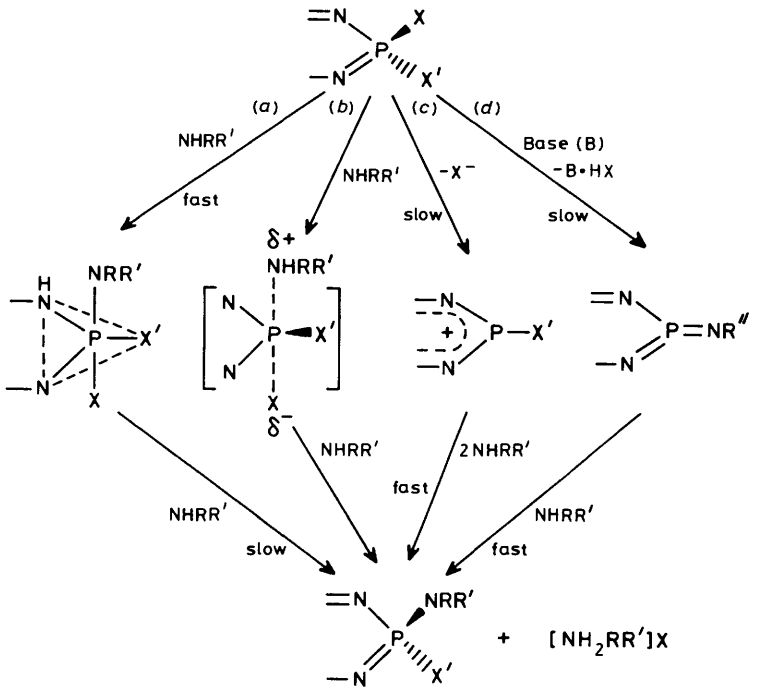

Figure 1. Generalized possible mechanisms for nucleophilic substitution reactions of halogenocyclophosphazenes: (*a*) X = X′ = Cl; (*b*) X = X′ = Cl; (*c*) X = Cl, X′ = NRR′; and (*d*) X = Cl, X′ = NHR″ (R, R′, R″ = H, alkyl, or aryl)

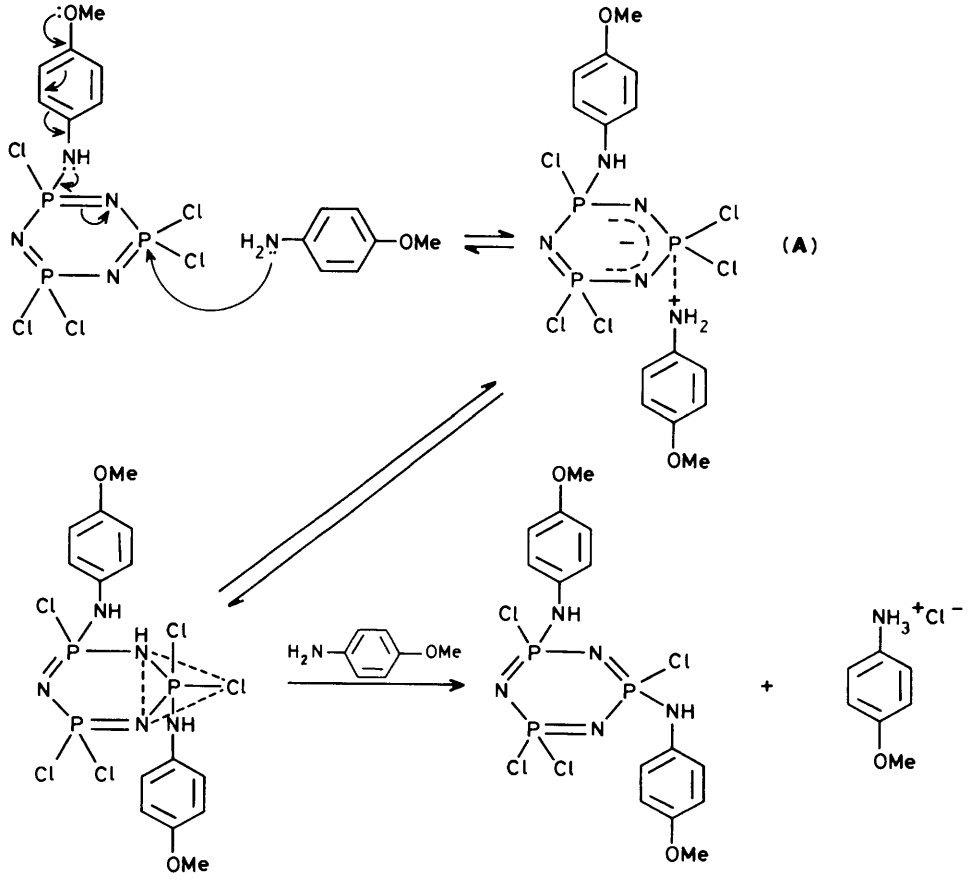

Figure 2. Stabilization of the five-co-ordinate intermediate by the *p*-anisidino group

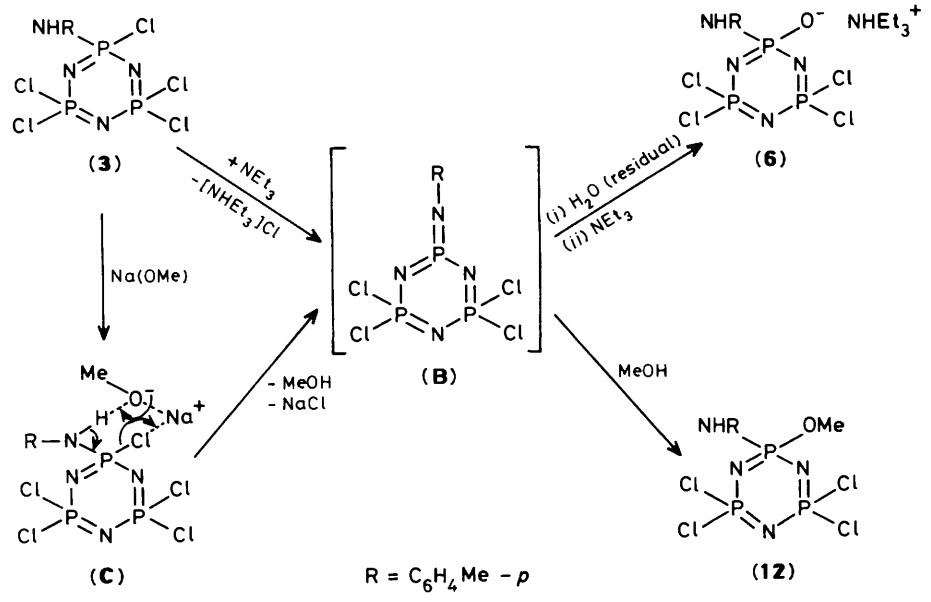

Figure 3. Generation and trapping of three-co-ordinate phosphorimidate type intermediate

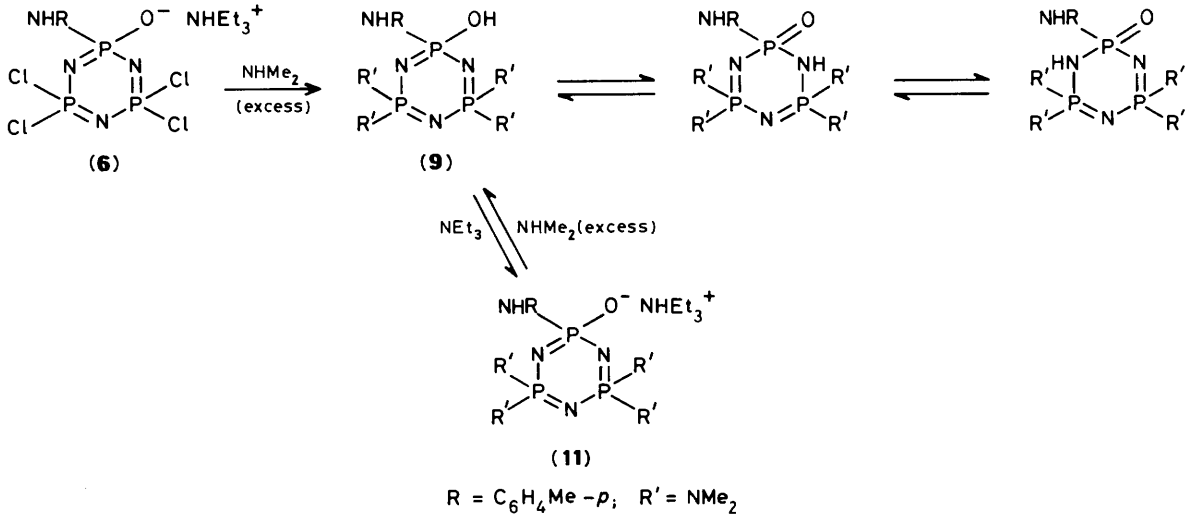

Figure 4. Reaction of (**6**) with dimethylamine followed by triethylamine

co-ordinate P^V intermediate in a rate-determining proton abstraction step, followed by rapid addition of the nucleophile to this reactive intermediate [Figure 1(*d*)]. This mechanism has essentially unimolecular characteristics; it is a special case of a unimolecular dissociative mechanism [Figure 1(*c*)] where there is a primary amino group on the phosphazene ring containing a ≡PCl(NHR) group. Although a proton abstraction mechanism has been previously suggested in cyclophosphazene chemistry,[4,12] the results of the present study provide the first kinetic evidence for such a mechanism. Recently, Harger[13] has demonstrated the operation of an E_1(c.b.) mechanism for the reaction of PR(O)Cl(NHBu^t) (R = Et, Pr^i, or Bu^t) with isopropyl- or t-butyl-amine.

In an attempt to isolate the three-co-ordinate P^V species postulated above [Figure 1(*d*)], the mono(arylamino) derivatives (**2**)—(**4**) were treated with an excess of triethylamine in thf in the absence of the reacting aromatic amine. The structures of the solid products obtained can be formulated as [$NHEt_3$][*gem*-$N_3P_3Cl_4$(NHR)(O)] [R = Ph (**5**), C_6H_4Me-*p* (**6**), or C_6H_4(OMe)-*p* (**7**)] from i.r. (Experimental section) and n.m.r. (Table 3) spectroscopic data. These products are formed even when moisture is strictly excluded to the extent possible and all operations are carried out under an inert atmosphere. Their formation is due to the high reactivity of the three-co-ordinate P^V species [(**B**) in Figure 3] which, in the absence of the reacting amine, picks up traces of moisture present in triethylamine and the solvent used or that which is adsorbed on the walls of the glass vessel. The hydroxy derivative thus formed reacts with triethylamine to form the respective salts. Such triethylammonium salts have been previously obtained (*a*) by the treatment of $N_3P_3Cl_6$ with benzoic acid and triethylamine[14] and (*b*) by the treatment of $N_3P_3Cl_6$ with salicylamide in the presence of triethylamine.[15]

The three-co-ordinate P^V species formed in the reaction of

$N_3P_3Cl_5(NHC_6H_4Me\text{-}p)$ (**3**) with an excess of triethylamine can also be trapped by methanol to afford the geminal derivative $N_3P_3Cl_4(NHC_6H_4Me\text{-}p)(OMe)$ (**12**). In the absence of triethylamine, compound (**3**) does not react with methanol in thf; the starting material (**3**) is recovered unchanged. Another interesting feature is that the reaction of compound (**3**) with one molar equivalent of sodium methoxide in thf yields the same geminal derivative (**12**). The P–NH protons of the primary amino substituent may participate in a hydrogen-bonded six-membered cyclic transition state with sodium methoxide [(**C**) in Figure 3] to generate the reactive three-co-ordinate P^V intermediate. This step is followed by the rapid addition of eliminated methanol to the intermediate to yield the geminal product (**12**). No non-geminal product has been identified in this reaction.

Attempts to isolate the ≡P=NR species (**B**) (Figure 3) either by using less moisture-sensitive solvents such as benzene or chloroform and a non-nucleophilic tertiary amine like 1,5-diazabicyclo[5.4.0]undecene[16] have been unsuccessful.

Dimethylaminolysis of the triethylammonium salts (**5**)—(**7**) is accompanied by loss of triethylamine and the product is a hydroxyphosphazene, *gem*-$N_3P_3(NHR)(OH)(NMe_2)_4$ [R = Ph (**8**), $C_6H_4Me\text{-}p$ (**9**), or $C_6H_4(OMe)\text{-}p$ (**10**)], which exists in its 'oxophosphazadiene' tautomeric form as shown in Figure 4. The presence of amino groups on the phosphazene ring enhances the basicity of ring nitrogen.[17–19] Therefore, the hydroxy proton migrates to the skeletal nitrogen instead of forming a salt with dimethylamine.

Treatment of the hydroxy compound (**9**) with an excess of triethylamine affords the salt $[NHEt_3][gem\text{-}N_3P_3(NHC_6H_4Me\text{-}p)(O)(NMe_2)_4]$ (**11**) which on treatment with an excess of dimethylamine yields (**9**). These interconversions are also shown in Figure 4.

The reaction of compound (**3**) with tri-n-butylamine to afford the three-co-ordinate P^V intermediate is faster than that of compound (**4**) with the same amine (see data in Table 2). This observation can be explained on the basis of the difference in the acidity of the NH protons. The electron-releasing power of the methoxy group is greater than that of the methyl group at the *para* position, resulting in the decreased acidity of the *p*-NH protons of $\equiv PCl[NHC_6H_4(OMe)\text{-}p]$. Therefore, proton abstraction becomes more facile for $\equiv PCl(NHC_6H_4Me\text{-}p)$ compared to $\equiv PCl[NHC_6H_4(OMe)\text{-}p]$.

The results of the present study can also readily explain the predominant formation of the geminal bis(anilino) derivative in the reaction of $N_3P_3Cl_6$ with aniline in benzene as reported by Shaw and co-workers.[20] Capon *et al.*[21] have shown that the reaction in aromatic solvents such as toluene includes a third-order term; the dehydrochlorination of the five-co-ordinate intermediate is brought about by the reacting amine itself acting as a base. Because of this third-order term, reactions in benzene are very slow even at the mono stage of chlorine replacement. Hence at the bis and subsequent stages, the associative pathway is further impeded with the result that the base-catalysed E_1(c.b.) dissociative pathway to yield the geminal bis(anilino) derivative becomes the only accessible route for the reaction.

Conclusions

All possible mechanisms of nucleophilic substitution reactions at a four-co-ordinate pentavalent phosphorus centre have now been realized in cyclophosphazene systems. Firm evidence for the formation of a three-co-ordinate P^V species has been obtained from kinetic data and by trapping with methanol as well as by the isolation of the unusual products (**5**)—(**7**). The mechanistic studies enable us to understand the combined role of the substituent present on the phosphazene ring, the attacking nucleophile, and the reaction medium on the nature of products formed in the nucleophilic substitution reactions of halogenocyclophosphazenes.

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