# Phosphorus–Nitrogen Compounds. Part XXXIV.[1] The Reactions of Hexachlorocyclotriphosphazatriene with Ethylamine: Comparisons with Isopropylamine and t-Butylamine

By **Rabindranath N. Das, Robert A. Shaw,* Barry C. Smith,** and **Michael Woods,** Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX

Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, reacts with ethylamine in boiling ether, benzene, or chloroform, to give the ethylamino-derivatives, $N_3P_3Cl_{6-n}(NHEt)_n$ ($n$ = 1, 2, 2, 3, 4, 6), a hydrochloride, $N_3P_3(NHEt)_6$,HCl, and an ethoxy-derivative, $N_3P_3Cl_2(NHEt)_3(OEt)$. Dimethylaminoethylamino-derivatives, $N_3P_3(NMe_2)_{6-n}(NHEt)_n$ [$n$ = 1, 2 (2 isomers), 3 (2 isomers), 4 (3 isomers), 5] and $N_3P_3(NMe_2)_2(NHEt)_3(OEt)$ are prepared from the chloroethylamino- and/or chlorodimethylamino-derivatives. The structures of the products are deduced from their $^1H$ n.m.r. spectra and their $pK'_a$ values. The replacement patterns of chlorine in $N_3P_3Cl_6$ by ethyl-, isopropyl-, and t-butyl-amines are compared and a hypothesis is put forward to rationalise the differences.

THE reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (I), with isopropylamine [2] and with t-butylamine [3] have been discussed in earlier parts of this series. This paper describes analogous reactions with ethylamine and compares the various replacement patterns. The ethylamino-derivatives (II)—(XXVIII) prepared in the course of this work are listed in Table 1, with their proposed structures.

TABLE 1

Ethylaminocyclotriphosphazatrienes

| | Compound | M.p. ($t$/°C) | Structure |
|---|---|---|---|
| (II) | $N_3P_3Cl_5(NHEt)$ | 34—35 | Nongem |
| (III) | $N_3P_3Cl_4(NHEt)_2$ | 85 | *trans*-Nongem |
| (IV) | $N_3P_3Cl_4(NHEt)_2$ | 98 | *cis*-Nongem |
| (V) | $N_3P_3Cl_3(NHEt)_3$ | 130—131 | Nongem |
| (VI) | $N_3P_3Cl_2(NHEt)_4$ | 126 | Gem |
| (VII) | $N_3P_3(NHEt)_6$ | 120—121 | Gem |
| (VIII) | $N_3P_3(NHEt)_6$,HCl | 202 | Gem |
| (IX) | $N_3P_3Cl_2(NHEt)_3(OEt)$ | 111 | 2,2:4,4,6:6 |
| (X) | $N_3P_3(NMe_2)_5(NHEt)$ | 94 | Nongem |
| (XI) | $N_3P_3(NMe_2)_4(NHEt)_2$ | 126 | *trans*-Nongem |
| (XII) | $N_3P_3(NMe_2)_4(NHEt)_2$,HCl | 150—160 | Nongem |
| (XIII) | $N_3P_3(NMe_2)_4(NHEt)_2$ | 74—76 | *cis*-Nongem |
| (XIV) | $N_3P_3(NMe_2)_4(NHEt)_2$,HCl | 155—157 | Nongem |
| (XV) | $N_3P_3(NMe_2)_3(NHEt)_3$ | 113 | Nongem |
| (XVI) | $N_3P_3(NMe_2)_3(NHEt)_3$,HCl | 182—184 | Nongem |
| (XVII) | $N_3P_3(NMe_2)_3(NHEt)_3$,HCl | 143—145 | Nongem |
| (XVIII) | $N_3P_3(NMe_2)_3(NHEt)_3$ | 85 | Gem |
| (XIX) | $N_3P_3(NMe_2)_2(NHEt)_4$ | 117 | Nongem |
| (XX) | $N_3P_3(NMe_2)_2(NHEt)_4$,HCl | 155—157 | Nongem |
| (XXI) | $N_3P_3(NMe_2)_2(NHEt)_4$ | 94—95 | Nongem |
| (XXII) | $N_3P_3(NMe_2)_2(NHEt)_4$,HCl | 162—164 | Nongem |
| (XXIII) | $N_3P_3(NMe_2)_2(NHEt)_4$ | 97 | Gem |
| (XXIV) | $N_3P_3(NMe_2)(NHEt)_5$ | 88 | Nongem |
| (XXV) | $N_3P_3(NMe_2)(NHEt)_5$,HCl | 170—175 | Nongem |
| (XXVI) | $N_3P_3(NMe_2)_2(NHEt)_3(OEt)$ | 90 | 2,2:4,4,6:6 |
| (XXVII) | $N_3P_3(NHEt)_4(OCH_2CF_3)_2$ | 85 | Gem |
| (XXVIII) | $N_3P_3(NHEt)_3(OEt)(OCH_2CF_3)_2$ | 78—79 | 2,2,4:4,6:6 |

Hexachlorocyclotriphosphazatriene (I) reacts with ethylamine in boiling ether, benzene, or chloroform to give six ethylamino-derivatives, $N_3P_3Cl_{6-n}(NHEt)_n$ ($n$ = 1—4 or 6) (II), (III), (V)—(VII); a hydrochloride, $N_3P_3(NHEt)_6$,HCl (VIII); and an ethoxy-derivative, $N_3P_3Cl_2(NHEt)_3(OEt)$ (IX). The second bisethylamino-derivative (IV) is obtained from its isomer (III) by reaction with dimethylamine hydrochloride in boiling chloroform. A prominent feature of the reactions of the hexachloride (I) with ethylamine (6 or 8 mol) is the formation of a sticky resinous material, m.p. >360°, which hinders the purification and diminishes the yields of tris- and tetrakis-ethylamino-derivatives. Comparable difficulties occur in reactions with ammonia [4,5] and methylamine.[6,7]

The chloroethylamino-derivatives (II)—(VII) react with an excess of dimethylamine to give dimethylamino-ethylaminocyclotriphosphazatrienes, $N_3P_3(NMe_2)_{6-n}(NHEt)_n$. The preparation of nine such derivatives [$n$ = 1, 2 (2 isomers), 3 (2 isomers), 4 (3 isomers), 5] either by this method, or by the reaction of chlorodimethylamino-derivatives, $N_3P_3Cl_{6-m}(NMe_2)_m$ [$m$ =

[1] Part XXXIII, C. D. Flint, E. H. M. Ibrahim, R. A. Shaw, B. C. Smith, and C. P. Thakur, *J. Chem. Soc.* (*A*), 1971, 3513.
[2] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1966, 1677.
[3] S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1965, 5032.
[4] M. C. Miller and R. A. Shaw, *J. Chem. Soc.*, 1963, 3233.
[5] G. R. Feistel and T. Moeller, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2731; W. Lehr, *Z. anorg. Chem.*, 1967, **356**, 18.
[6] W. Lehr, *Z. anorg. Chem.*, 1967, **352**, 27.
[7] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1965, **4**, 890.

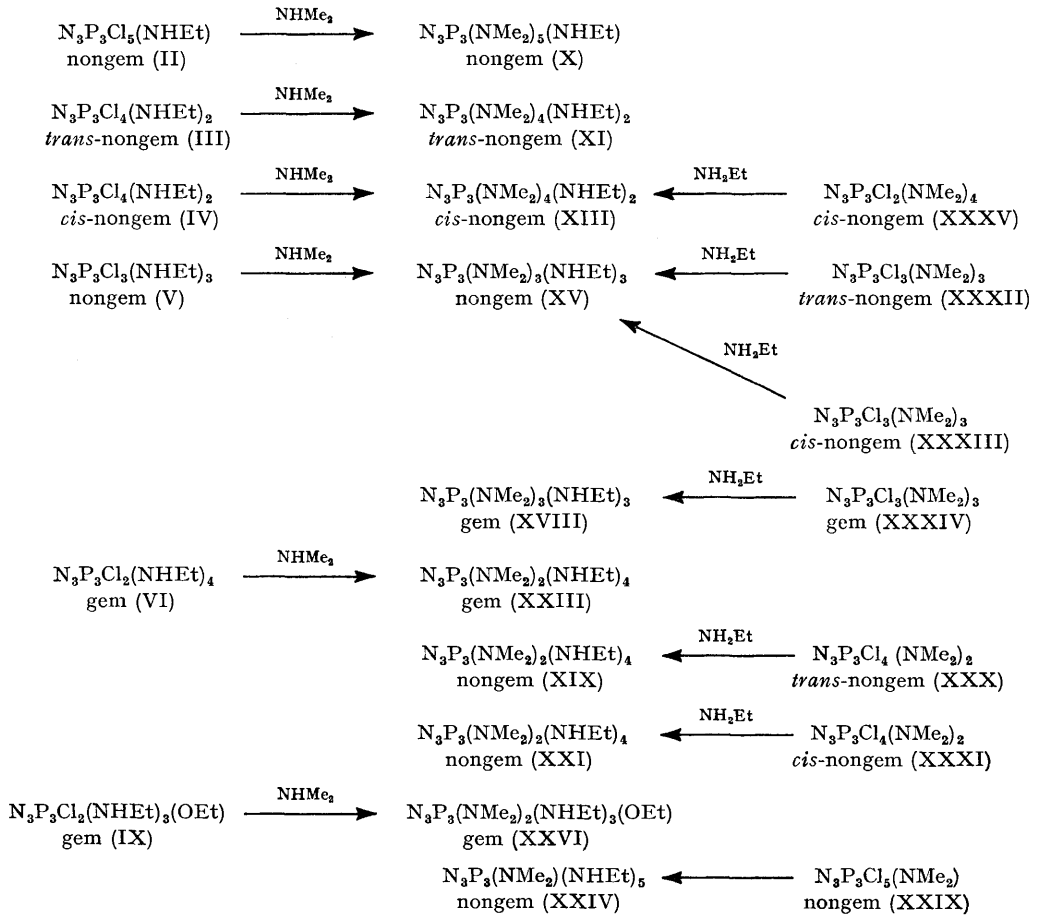
TABLE 2

$^1$H N.m.r. data for ethylaminocyclotriphosphazatrienes ($CCl_4$ solution)

| | | NHEt | | | $NMe_2$ | | |
|---|---|---|---|---|---|---|---|
| | Compound | $\tau_{CH_3}$ | $\tau_{CH_2}$ † | $\tau_{NH}$ ‡ | $\tau_{NMe_2}$ | $J^*_{P-H}$ | Structure |
| (II) | $N_3P_3Cl_5(NHEt)$ | 8·71 | 6·84 | 6·4 | | | Nongem |
| (III) | $N_3P_3Cl_4(NHEt)_2$ | 8·72 | 6·84 | 6·2 | | | *trans*-Nongem |
| (IV) | $N_3P_3Cl_4(NHEt)_2$ | 8·73 | 6·89 | 6·2 | | | *cis*-Nongem |
| (V) | $N_3P_3Cl_3(NHEt)_3$ | 8·75 | 6·88 | 6·4 | | | Nongem |
| (VI) | $N_3P_3Cl_2(NHEt)_4$ | 8·83 | 7·10 | 7·3 | | | Gem |
| (VII) | $N_3P_3(NHEt)_6$ | 8·89 | 7·17 | 7·4 | | | Gem |
| (IX) | $N_3P_3Cl_2(NHEt)_3(OEt)$ | 8·83 | 7·09 | § | | | 2,2:4,4,6:6 |
| | | 8·73 [a] | 6·09 [b] | | | | |
| (X) | $N_3P_3(NMe_2)_5(NHEt)$ | 8·90 | 7·1 | 8·2 | 7·43, 7·46 | 12·0, 11·7 | Nongem |
| | | | | | 7·48 | 11·7 | |
| (XI) | $N_3P_3(NMe_2)_4(NHEt)_2$ | 8·90 | 7·2 | 8·2 | 7·45, 7·48 | 12·2, 11·1 | *trans*-Nongem |
| (XIII) | $N_3P_3(NMe_2)_4(NHEt)_2$ | 8·90 | 7·2 | 8·0 | 7·42, 7·42 | 12·2, 11·2 | *cis*-Nongem |
| | | | | | 7·47 | 11·0 | |
| (XV) | $N_3P_3(NMe_2)_3(NHEt)_3$ | 8·90 | 7·1 | 8·0 | 7·43 | 12·2 | Nongem |
| (XVIII) | $N_3P_3(NMe_2)_3(NHEt)_3$ | 8·90 | 7·2 | 7·8 | 7·44, 7·46 | 11·8, 11·0 | Gem |
| | | | | | 7·48 | 10·8 | |
| (XIX) | $N_3P_3(NMe_2)_2(NHEt)_4$ | 8·90 | 7·1 | 7·7 | 7·45 | 11·5 | Nongem |
| (XXI) | $N_3P_3(NMe_2)_2(NHEt)_4$ | 8·88 | 7·14 | 7·8 | 7·42 | 11·0 | Nongem |
| (XXIII) | $N_3P_3(NMe_2)_2(NHEt)_4$ | 8·90 | 7·09 | 7·7 | 7·47 | 11·0 | Gem |
| (XXIV) | $N_3P_3(NMe_2)(NHEt)_5$ | 8·88 | 7·12 | 7·7 | 7·43 | 11·0 | Nongem |
| (XXVI) | $N_3P_3(NMe_2)_2(NHEt)_3(OEt)$ | 8·89 | 7·1 | 7·7 | 7·43, 7·46 | 10·8, 11·0 | 2,2:4,4,6:6 |
| | | 8·77 [a] | 6·19 [b] | | | | |

† Some of the methylene signals gave broad bands and therefore some $\tau$ values are quoted to two significant figures only. ‡ Centre of broad band. § Hidden by N–$CH_2$ proton signal, hence positioned at $\tau$ *ca.* 7·0—7·3.

[a] $OCH_2CH_3$. [b] $OCH_2CH_3$.




SCHEME 1 The preparation of dimethylaminoethylaminocyclotriphosphazatrienes. (Hydrochlorides are omitted.)

1, 2 (2 isomers), 3 (3 isomers), 4] of known structure,[8,9] with an excess of ethylamine is summarised by Scheme 1. There are also seven hydrochlorides, $N_3P_3(NMe_2)_{6-n}(NHEt)_n,HCl$ [$n$ = 2 (2 isomers), 3 (2 isomers), 4 (2 isomers), 5], which give free bases on treatment with triethylamine in benzene. The chloroethoxy-derivative, $N_3P_3Cl_2(NHEt)_3(OEt)$ (IX), is converted similarly into a dimethylaminoethoxy-derivative, $N_3P_3(NMe_2)_2(NHEt)_3(OEt)$, (XXVI). Structural information about some chloroethylamino-derivatives can be inferred from the reactions outlined in Scheme 1, as geminal to nongeminal rearrangements are unknown in phosphazene chemistry. For example, the bisethylamino-derivatives (III) and (IV) and the trisethylamino-derivative (V) must be nongeminal; whereas the tetrakisethylamino-derivative (VI) must be geminal. More information about the structures of ethylamino-derivatives are obtained from their $^1$H n.m.r. spectra, which are summarised in Table 2.

Inspection of the chemical shift data of the protons of the ethylamino-derivatives reveal the following trends: (*a*) $-NHCH_2CH_3$: a steady increase for compounds (II)—(V) from $\tau$ 8·71—8·75, then a sudden increase to $\tau$ 8·83—8·90 for the compounds (VI), (VII), and (IX); (*b*) $NHCH_2CH_3$: a somewhat more pronounced trend in the same direction, $\tau$ 6·84—6·89 and $\tau$ 7·09—7·20, for the above two sets of compounds; (*c*) $NHCH_2CH_3$: three regions of absorptions, (i) $\tau$ 6·2—6·4 [compounds (II)—(V)], (ii) $\tau$ ~7·3 [compounds (VI) and (IX), no chlorine atom geminal to an amino-group], and (iii) $\tau$ 7·7—8·2 (the fully aminolysed compounds).

The above trends support the nongeminal assignments for compounds (II)—(V). The shielding of the methylene protons is greater for the *cis*-compound (IV) than for its *trans*-analogue (III) (for other structural evidence, see below). This represents another example of the '*cis*-effect.'[10] The increase in deshielding observed for the N–H protons of the fully aminolysed compounds, $N_3P_3(NHEt)_{6-n}(NMe_2)_n$, as $n$ varies from 5 to 1, probably indicates that increasing numbers of N–H protons compete to form hydrogen bonds with a fixed number of lone-pairs of electrons on nitrogen atoms.

The tetrachlorobisethylamino-isomer, $N_3P_3Cl_4(NHEt)_2$ (III), reacts with dimethylamine to give $N_3P_3(NMe_2)_4(NHEt)_2$ (XI), whose dimethylamino $^1$H n.m.r. spectrum shows two overlapping doublets (with virtual coupling) of approximately equal intensity indicating a *trans*-nongeminal structure, and a hydrochloride (XII). The second tetrachlorobisethylamino-isomer (IV) forms $N_3P_3(NMe_2)_4(NHEt)_2$ (XIII), whose dimethylamino $^1$H n.m.r. spectrum shows three overlapping doublets with virtual coupling indicating a *cis*-nongeminal structure, and a hydrochloride (XIV). This base (XIII) is prepared also from *cis*-nongeminal $N_3P_3Cl_2(NMe_2)_4$ (XXXV). It is inferred that the isomers (III) and (IV) have *trans*- and *cis*-nongeminal structures respectively. This is consistent with their order of elution in column chromatography: *trans* before *cis*; which appears to be general for cyclotriphosphazatrienes[8,10] and cyclodiphosphazanes.[1,11]

The $^1$H n.m.r. spectrum at 100 MHz does not establish whether nongeminal-$N_3P_3Cl_3(NHEt)_3$ (V) has a *cis*- or *trans*-structure. The methyl proton signal appears as one triplet, but the signals of β-methyl protons of primary alkylaminophosphazenes are less sensitive to changes in chemical environment than those of secondary alkylaminophosphazenes (probably because of steric effects), *e.g.*, *cis*- and *trans*-$N_3P_3Cl_3(NEt_2)_3$ are distinguished easily by their β-methyl proton signals.[12] The methylene proton signal of compound (V) is broad and the contribution of the intense virtual coupling to the linewidth is difficult to estimate. The mass spectrum confirms that this is an authentic trichlorotrisethylamino-derivative: *m/e*, obs. 371·9871; calc. 371·9871.

The nongeminal trichlorotrisethylamino-derivative (V) reacts with dimethylamine to give nongeminal-$N_3P_3(NMe_2)_3(NHEt)_3$ (XV), whose dimethylamino $^1$H n.m.r. spectrum consists of one doublet with virtual coupling, and a hydrochloride (XVI). There are important reasons for restraint in assigning configurations to these derivatives (V), (XV): (*a*) the absence of multiplicity in signals does not necessarily indicate identical chemical environments [*cf.* compounds (IX), (XIX), and (XXI)], and there is some indication that ethylamino-derivatives present considerable difficulties in this respect (see below); (*b*) *cis*–*trans*-isomerisation can occur during aminolysis. For example, the reactions of *cis*- or *trans*-nongeminal $N_3P_3Cl_3(NMe_2)_3$ (XXIII) or (XXII) with an excess of ethylamine appear to give two hydrochlorides of different m.p. (XVI) or (XVII) respectively, both of which give the base (XV) on treatment with triethylamine in benzene. The formation of two hydrochlorides by one base occurs also in the isopropylamino-series[2] and this topic will be considered at greater length elsewhere.

Basicity measurements of the chloroethylamino-derivatives[13] are listed in Table 3. The monoethylamino-(II) and bisethylamino-(III), (IV) derivatives have $pK'_a$ values of $<-6$. The observed basicity of the nongeminal trisethylamino-derivative (V), $pK'_a$ −4·9, is close to −4·7 calculated from known substituent constants,[14] and considerably lower than the value estimated for geminal-$N_3P_3Cl_3(NHEt)_3$, $pK'_a$ −3·0.

Geminal-$N_3P_3Cl_3(NMe_2)_3$ (XXXIV) reacts with ethylamine to give geminal-$N_3P_3(NMe_2)_3(NHEt)_3$ (XVIII), whose dimethylamino $^1$H n.m.r. spectrum shows three overlapping doublets.

[8] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.
[9] R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 1965, 7193.
[10] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 908.
[11] E. H. M. Ibrahim, R. A. Shaw, B. C. Smith, C. P. Thakur, M. Woods, G. J. Bullen, J. S. Rutherford, P. A. Tucker, T. S. Cameron, K. D. Howlett, and C. K. Prout, *Phosphorus*, 1972, **7**, 153.
[12] R. N. Das, R. A. Shaw, and B. C. Smith, unpublished results.
[13] D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 1964, 2387.
[14] D. Feakins, R. A. Shaw, P. Watson, and S. N. Nabi, *J. Chem. Soc.* (*A*), 1969, 2468.

TABLE 3
Basicities of ethylaminocyclotriphosphazatrienes in nitrobenzene at 20 °C

| | Compound | p$K'_a$ | Structure |
|---|---|---|---|
| (II) | $N_3P_3Cl_5(NHEt)$ | $<-6$ | Nongem |
| (III) | $N_3P_3Cl_4(NHEt)_2$ | $<-6$ | *trans*-Nongem |
| (IV) | $N_3P_3Cl_4(NHEt)_2$ | $<-6$ | *cis*-Nongem |
| (V) | $N_3P_3Cl_3(NHEt)_3$ | $-4.9$ | Nongem |
| (VI) | $N_3P_3Cl_2(NHEt)_4$ | $+3.2$ | Gem |
| (VII) | $N_3P_3(NHEt)_6$ | $+8.2$ | Gem |
| (IX) | $N_3P_3Cl_2(NHEt)_3(OEt)$ | $+1.4$ | 2,2:4,4,6:6 |
| (XXVII) | $N_3P_3(NHEt)_4(OCH_2CF_3)_2$ | $+3.7$ | Gem |
| (XXVIII) | $N_3P_3(NHEt)_3(OEt)$-$(OCH_2CF_3)_2$ | $+2.9$ | 2,2,4:4:6,6 |

The $^{31}P$ n.m.r. spectrum [15] of geminal-$N_3P_3Cl_2(NHEt)_4$ (VI) contains signals characteristic of $\equiv PCl_2$ and $\equiv P(NHEt)_2$ groups in the ratio 1 : 2. The basicity, p$K'_a$ +3·2, is similar to that of other geminal tetrakis-alkylamino-derivatives: [16] *cf.* geminal-$N_3P_3Cl_2(NHPr^i)_4$ +3·4, geminal-$N_3P_3Cl_2(NHBu^t)_4$ +3·5. The reaction with dimethylamine gives geminal-$N_3P_3(NMe_2)_2(NHEt)_4$ (XXIII), whose dimethylamino $^1H$ n.m.r. spectrum consists of one doublet without virtual coupling (*cf.* refs. 2, 3). The two nongeminal tetrachlorobisdimethylamino-derivatives (XXX) and (XXXI) react with ethylamine to give the nongeminal isomers $N_3P_3(NMe_2)_2$-$(NHEt)_4$ (XIX) and (XXI) and their hydrochlorides (XX) and (XXII).

An ethoxy-derivative, $N_3P_3Cl_2(NHEt)_3(OEt)$ (IX), was the major product of the reaction of the hexachloride (I) with ethylamine (8 mol) in boiling chloroform. Commercial chloroform contains ethanol as a stabiliser, and calculations suggest that, after replacement of the first three chlorine atoms, this reaction mixture contained approximately the same number of equivalents of ethanol as of ethylamine. This is probably the first example of competitive solvolysis in cyclophosphazene chemistry, although products containing ethoxy-groups have been isolated from reactions of phenylphosphonic and phenylphosphonothioic dichlorides with dibenzylamine in chloroform.[17] Low yields of the ethoxy-derivative (IX) are obtained also from reactions of the hexachloride (I) with ethylamine in ether.

The previous assumption [18] that compound (IX) might be a nongeminal tetrakisethylamino-derivative is incorrect. A more detailed study indicates that this compound contains an ethoxy-group. The mass spectrum shows clearly the molecular ion, $N_3P_3Cl_2(NHEt_3)(OEt)^+$; *m/e*, obs. 382·0517; calc. 382·0525. The i.r. spectrum contains a strong band at 1030 $cm^{-1}$, characteristic of P–O–Et vibrations.[19] The basicity agrees well with that calculated from substituent constants for geminal-$N_3P_3Cl_2(NHEt)_3(OEt)$: p$K'_a$, obs. +1·4; calc. +1·3.*

* $\alpha_{NHEt}$ is unchanged from the published value,[14] as compound (IX) was not used in its calculation. $\alpha_R \approx 2\nu_R$; [14,20] hence p$K'_a$ $N_3P_3(OEt)_6$ $(-0·2)$ − p$K'_a$ $N_3P_3(OMe)_6$ $(-1·9) = 1·7 \approx 5\alpha_{OEt} - 5\alpha_{OMe}$. Hence, as $\alpha_{OMe} = 3·6$, $\alpha_{OEt} \approx 3·9$.

[15] R. Keat, R. A. Shaw, and M. Woods, unpublished results.
[16] D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1831.
[17] J. D. Healy, R. A. Shaw, B. C. Smith, C. P. Thakur, and M. Woods, unpublished results.

The $^1H$ n.m.r. spectrum in deuteriochloroform consists of three groups of signals of relative intensities 12 : 9 : 2, which are assigned as follows: (*a*) $OCH_2CH_3$ and $NHCH_2CH_3$, two overlapping triplets at $\tau$ 8·70 and 8·84 of relative intensities 1 : 3; (*b*) $NHCH_2CH_3$, a broad asymmetric hump at *ca.* $\tau$ 7·0, which resolves into a multiplet of six lines (two overlapping quartets) of reduced intensity when the solution is shaken with deuterium oxide; and (*c*) $OCH_2CH_3$, a complex multiplet at $\tau$ 6·03. The $^1H$ n.m.r. spectrum at 220 MHz shows the methyl protons of the ethoxy- and ethylamino-groups as separate triplets, but the three chemically different ethylamino-groups cannot be distinguished, *cf.* discussion of nongeminal-$N_3P_3Cl_3(NHEt)_3$ (V), above.

This ethoxy-derivative (IX) reacts with dimethylamine to give $N_3P_3(NMe_2)_2(NHEt)_3(OEt)$ (XXVI), *m/e*: obs. 400; calc. 400, whose $^1H$ n.m.r. spectrum in deuteriochloroform consists of five groups of signals of relative intensities 12 : 3 : 12 : 6 : 2; (*d*) $OCH_2CH_3$ and $NHCH_2CH_3$, two overlapping triplets at $\tau$ 8·72 and 8·88 of relative intensities 1 : 3; (*e*) $NHCH_2CH_3$, a broad hump at *ca.* $\tau$ 7·85 which disappears on shaking with deuterium oxide; (*f*) $N(CH_3)_2$, a doublet at $\tau$ 7·38; (*g*) $NHCH_2CH_3$, a complex multiplet at $\tau$ 7·05, which sharpens on shaking with deuterium oxide; and (*h*) $OCH_2CH_3$, a complex multiplet at $\tau$ 6·05. The dimethylamino-proton signals appear as a doublet because of coupling with phosphorus, and the absence of virtual coupling suggests that both dimethylamino-groups are attached to the same phosphorus atom.[2,3] The corresponding signals from carbon tetrachloride solutions, which appear as two overlapping doublets without virtual coupling ($^3J^*_{P-H}$ 10·8, 11·0 Hz), reveal that the geminal dimethylamino-groups are in different chemical environments.

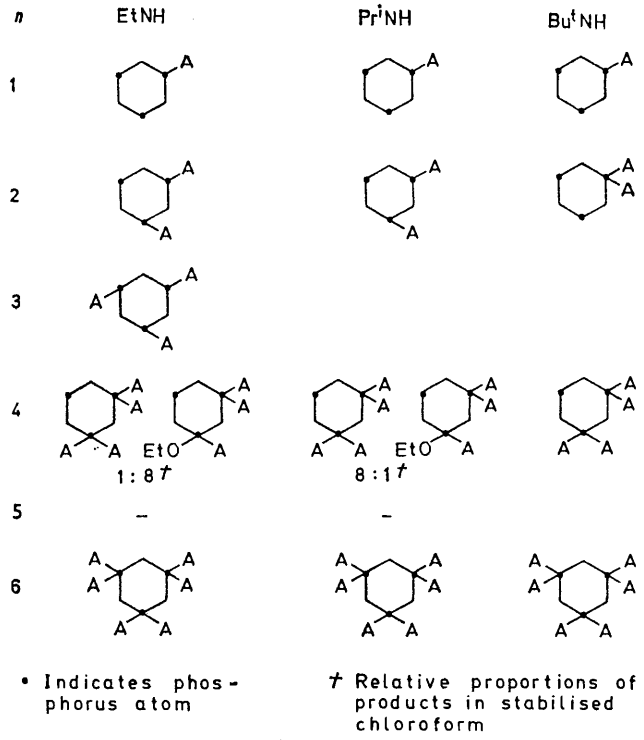
The geminal tetrakisethylamino-derivative (VI) and the ethoxy-derivative (IX) react with sodium trifluoroethoxide in benzene [21] to give $N_3P_3(NHEt)_4(OCH_2CF_3)_2$ (XXVII) and $N_3P_3(NHEt)_3(OEt)(OCH_2CF_3)_2$ (XXVIII) respectively. The $^{19}F$ n.m.r. spectra of these derivatives: one triplet, $^3J_{H-F}$ 8·5 Hz (XXVII); and two overlapping triplets, $^3J_{H-F}$ 8·5, 8·6 Hz (XXVIII), indicate their structural differences. The larger range of chemical shifts in $^{19}F$ n.m.r. spectra may provide a more sensitive method for distinguishing between the similar environments encountered in some phosphazene derivatives.

The formation of the dichlorotrisethylaminomonoethoxy-derivative (IX) led us to look more closely at the reactions of the hexachloride (I) with isopropylamine and, in particular, at the supposedly nongeminal dichlorotetrakisisopropylamino-derivative, which had been prepared in boiling chloroform.[2] The $^1H$ n.m.r. spectrum shows the presence of an ethoxy-group. The mass

[18] R. A. Shaw, *Chem. and Ind.*, 1967, 1737; *Rec. Chem. Progr.*, 1967, **28**, 243; *Endeavour*, 1968, **27**, 74.
[19] L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, 1964, **20**, 489.
[20] D. Feakins, W. A. Last, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc.* (*A*), 1969, 196.
[21] M. R. Bond, R. A. Shaw, and M. Woods, unpublished results.

spectrum shows a peak at *m/e* 424, corresponding to the molecular ion $N_3P_3Cl_2(NHPr^i)_3(OEt)^+$. The geminal positions of the two chlorine atoms are confirmed by the basicity: $pK'_a$, found [16] +1·0; calc. +1·3.* Thus, the 'dichloroisopropylamino-derivative,' m.p. 88·5, is identified as 2,2:4,4,6:6-$N_3P_3Cl_2(NHPr^i)_3(OEt)$ (see Appendix).

In the aminolysis of a chlorocyclophosphazene, the nucleophilicity of a given amine in a given medium stays constant, but the electrophilicity of the phosphazene substrate changes with progressive aminolysis. Qualitative observations suggest that the rates of reaction of the hexachloride (I) with the primary amines, ethylamine, isopropylamine, and t-butylamine, decrease with increasing bulk of alkyl group. The replacement patterns with these three amines are compared in Scheme 2.

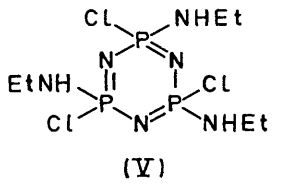



SCHEME 2

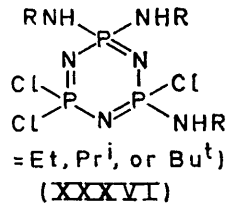
Main reaction products obtained from the reaction of $N_3P_3Cl_6$ with primary amines AH in organic solvents to give $N_3P_3Cl_{6-n}A_n$

Initial nucleophilic attack by an amine at a $\equiv PCl_2$ group gives moderate yields of all three monoalkylamino-derivatives, $N_3P_3Cl_{6-n}(NHR)_n$ ($n = 1$). The two more reactive amines ($NH_2Et$, $NH_2Pr^i$) then react with a second $\equiv PCl_2$ group to give nongeminal bisalkylamino-derivatives ($n = 2$). t-Butylamine forms only a geminal bisalkylamino-derivative. It is reported elsewhere [22] that the products obtained from this type of reaction depend on the attacking amine rather than on the amino-substituent of the phosphazene-derivative. Thus, ethylamine reacts with $N_3P_3Cl_5$·$NHBu^t$ at a $\equiv PCl_2$ group to give nongeminal-$N_3P_3Cl_4(NHEt)(NHBu^t)$, whereas t-butylamine reacts with $N_3P_3Cl_5$·NHEt to give geminal-$N_3P_3Cl_4(NHEt)(NHBu^t)$.[22] Recent kinetic data by Goldschmidt and Licht [23] also indicate the dominant role of the nucleophile in the formation of *trans*-nongeminal $N_3P_3Cl_4(NMe_2)(NHMe)$.

Replacement of a third chlorine atom by ethylamine occurs at the remaining $\equiv PCl_2$ group to give a trace of




(V)




(R = Et, Pr^i, or Bu^t)

(XXXVI)

nongeminal-$N_3P_3Cl_3(NHEt)_3$ (V). This is the only trisalkylamino-derivative which has been isolated from reactions with primary aliphatic amines. Yet it is clear that all three amines must form substantial amounts of geminal trisalkylamino-derivatives as reactive intermediates [*e.g.* (XXXVI)] in the formation of the geminal tetrakisalkylamino-derivatives, and (with ethylamine and isopropylamine) the geminal dichlorotrisalkylamino-monoethoxy-derivatives. Nongeminal tetrakisalkylamino-derivatives have not been observed.

The reaction patterns of the hexachloride (I) with secondary amines, *e.g.* dimethylamine [8] and piperidine,[10] are predominantly nongeminal: reaction at a $\equiv PCl_2$ centre is preferred to reaction at $\equiv PClA$ (A = $NMe_2$, pip). In contrast, geminal replacement is predominant at all stages of the reactions with primary amines that react slowly whether for steric reasons, *e.g.*, t-butylamine,[3] or polar reasons, *e.g.* aniline.[24] Geminal replacement occurs also at later stages of the reactions with the more reactive primary amines, *e.g.* ethylamine, and isopropylamine,[2] when the phosphazene substrate has become less electrophilic.

Some special features pertaining to primary amines must enhance their reactivity with $\equiv PCl$·NHR (or $\equiv PCl$·$NR_2$) groups, relative to that with $\equiv PCl_2$ groups. These reactions probably involve six-membered, cyclic hydrogen-bonded complexes (*A*, *B*, or *C*; R = Alk or Ar, R′ = H or Alk, R″ = Alk or Ar), as intermediates. The observation that aniline [25] and t-butylamine [26] prefer to react at a $\equiv PCl$·$NMe_2$ rather than at a $\equiv PCl_2$ site suggests that N–H bonds of the nucleophile rather than of the substituent play the dominant role.

Proton abstraction at the N–H bond by base can undoubtedly occur (*e.g.* exchange with $D_2O$). We have

* The value $\alpha_{NHPr^i} = 5·8$ previously published [14] is in error as the observed basicity of $N_3P_3Cl_2(NHPr^i)_3(OEt)$ [ascribed earlier [2] erroneously to the structure ng. $N_3P_3Cl_2(NHPr^i)_4$], was used in its calculation. A reassessment of $\alpha_{NHPr^i}$ from other compounds suggests a value of 6·0 (*cf.* $\alpha_{NHC_6H_{11}} = 6·0$ [14]).

[22] R. Keat and R. A. Shaw, *Angew. Chem. Internat. Edn.*, 1968, **7**, 272.
[23] J. M. E. Goldschmidt and E. Licht, *J.C.S. Dalton*, 1972, 728, 732.
[24] V. B. Desai, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1970, 2023.
[25] V. B. Desai, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.* (*A*), 1969, 1977.
[6] R. Keat and R. A. Shaw, unpublished results.

TABLE 4

Preparation of ethylaminocyclotriphosphazatrienes †

| Phosphazatriene | | | Amine | | | Solvent ‡ | | Yields | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (g) | (mmol) | | (g) | (mmol) | | (ml) | (g) | | (%) |
| (I) | 20·0 | 57 | $NH_2Et$ | 5·2 | 116 | $Et_2O$ | 450 | 20·4 | (I) | 8 |
| | | | | | | | | | (II) | 61 |
| | | | | | | | | | (III) | 6 |
| (I) | 20·0 | 57 | $NH_2Et$ | 10·4 | 231 | $Et_2O$ | 590 | 21·0 | (II) | 20 |
| | | | | | | | | | (III) | 72 |
| (I) | 20·0 | 57 | $NH_2Et$ | 15·4 | 342 | $Et_2O$ | 650 | 18·5 * | (III) | 8 |
| | | | | | | | | | (V) | 13 |
| | | | | | | | | | (IX) | 4 |
| (I) | 20·0 | 57 | $NH_2Et$ | 20·7 | 460 | $Et_2O$ | 650 | 17·3 * | (III) | 17 |
| | | | | | | | | | (V) | 1 |
| | | | | | | | | | (IX) | 1 |
| (I) | 20·0 | 57 | $NH_2Et$ | 20·7 | 460 | $CHCl_3$ | 550 | 17·6 * | (III) | 0·5 |
| | | | | | | | | | (V) | Trace |
| | | | | | | | | | (VI) | 2 |
| | | | | | | | | | (IX) | 16 |
| (I) | 10·0 | 29 | $NH_2Et$ | 35·0 | 778 | PhH | 200 | 9·0 | (VII) | 52 |
| | | | | | | | | | (VIII) | 20 |
| (II) | 2·0 | 6 | $NHMe_2$ | 3·5 | 78 | $CHCl_3$ | 150 | 1·9 | (X) | 86 |
| (III) | 3·0 | 8 | $NHMe_2$ | 5·0 | 111 | $CHCl_3$ | 150 | 2·1 | (XI) | 65 |
| | | | | | | | | 0·5 | (XII) | 14 |
| (III) | 17·0 | 46 | $NH_2Me_2Cl$ | 17·0 | 209 | $CHCl_3$ | 300 | 8·5 | (III) | 50 |
| | | | | | | | | 0·9 | (IV) | 5 |
| (IV) | 1·4 | 4 | $NHMe_2$ | 2·0 | 44 | PhH | 100 | 0·9 | (XII) | 60 |
| | | | | | | | | 0·4 | (XIV) | 24 |
| (V) | 1·0 | 3 | $NHMe_2$ | 1·2 | 27 | PhH | 50 | 0·5 | (XV) | 47 |
| | | | | | | | | 0·35 | (XVI) | 30 |
| (VI) | 1·0 | 3 | $NHMe_2$ | 1·0 | 22 | $CHCl_3$ | 100 | 0·5 | (XXIII) | 48 |
| (VIII) | 2·0 | 5 | $NEt_3$ | 2·0 | 20 | PhH | 30 | 1·5 | (VII) | 83 |
| (IX) | 0·9 | 2·7 | $NHMe_2$ | 2·0 | 44 | $CHCl_3$ | 25 | 0·85 | (XXVI) | 88 |
| (XXIX) | 1·8 | 5 | $NH_2Et$ | 5·0 | 110 | $CHCl_3$ | 40 | 1·1 | (XXIV) | 55 |
| | | | | | | | | 0·45 | (XXV) | 21 |
| (XXX) | 2·5 | 7 | $NH_2Et$ | 3·0 | 67 | $CHCl_3$ | 200 | 1·7 | (XIX) | 63 |
| | | | | | | | | 0·9 | (XX) | 30 |
| (XXXI) | 1·0 | 3 | $NH_2Et$ | 3·0 | 67 | PhH | 100 | 0·49 | (XXI) | 47 |
| | | | | | | | | 0·21 | (XXII) | 24 |
| (XXXII) | 2·0 | 5 | $NH_2Et$ | 2·4 | 53 | PhH | 100 | 1·4 | (XV) | 66 |
| | | | | | | | | 0·4 | (XVI) | 17 |
| (XXXIII) | 1·1 | 3 | $NH_2Et$ | 1·3 | 29 | PhH | 100 | 0·4 | (XV) | 36 |
| | | | | | | | | 0·3 | (XVII) | 25 |
| (XXXIV) | 3·2 | 9 | $NH_2Et$ | 4·0 | 89 | $CHCl_3$ | 150 | 2·7 | (XVIII) | 80 |
| (XXXV) | 3·0 | 8 | $NH_2Et$ | 2·8 | 62 | PhH | 200 | 2·4 | (XIII) | 75 |
| | | | | | | | | 0·03 | (XIV) | 1 |

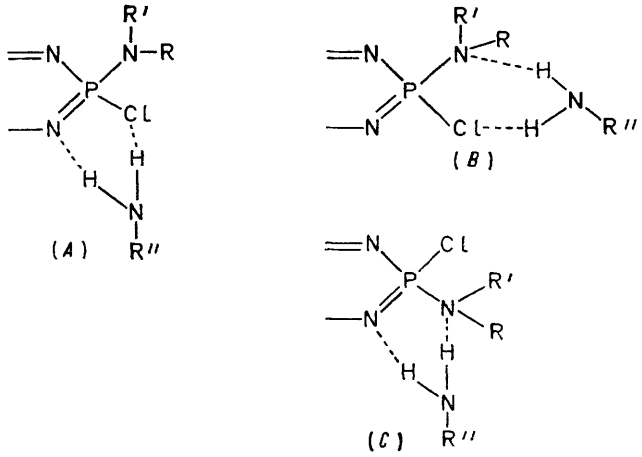
* Large amount of resinous material (m.p. >360) obtained. † See also Scheme 1. ‡ Reflux temperatures were used after initial addition of amine at ~0 °C.

TABLE 5

Analysis of ethylaminocyclotriphosphazatrienes

| | Found (%) | | | | | Requires (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C | H | Cl | N | Formula | C | H | Cl | N |
| (II) | 6·8 | 1·8 | 49·8 | 15·6 | $C_2H_6Cl_5N_4P_3$ | 6·7 | 1·7 | 49·7 | 15·7 |
| (III) | 13·2 | 3·4 | 38·7 | 18·9 | $C_4H_{12}Cl_4N_5P_3$ | 13·1 | 3·3 | 38·9 | 19·2 |
| (IV) | 13·3 | 3·3 | 38·8 | 19·2 | $C_4H_{12}Cl_4N_5P_3$ | 13·1 | 3·3 | 38·9 | 19·2 |
| (V) | 19·5 | 4·8 | 29·5 | 22·4 | $C_6H_{18}Cl_3N_6P_3$ | 19·3 | 4·8 | 29·6 | 22·4 |
| (VI) | 25·1 | 6·1 | 18·4 | 25·5 | $C_8H_{24}Cl_2N_7P_3$ | 25·1 | 6·2 | 18·5 | 25·7 |
| (VII) | 36·3 | 9·2 | | 31·5 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (VIII) | 33·8 | 8·6 | 8·0 | 28·6 | $C_{12}H_{37}ClN_9P_3$ | 33·0 | 8·5 | 8·1 | 29·0 |
| (IX) | 24·9 | 6·2 | | 21·9 | $C_8H_{23}Cl_2N_6OP_3$ | 24·8 | 6·2 | 18·5 | 21·9 |
| (X) | 36·2 | 9·4 | | 31·5 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XI) | 36·0 | 9·0 | | 31·5 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XII) | 32·7 | 8·3 | 8·0 | | $C_{12}H_{37}ClN_9P_3$ | 33·0 | 8·5 | 8·1 | 29·0 |
| (XIII) | 35·9 | 9·1 | | 31·4 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XIV) | 33·0 | 8·7 | 7·9 | 28·7 | $C_{12}H_{37}ClN_9P_3$ | 33·0 | 8·5 | 8·1 | 29·0 |
| (XV) | 36·1 | 8·9 | | 31·4 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XVI) | 33·1 | 8·6 | 8·0 | | $C_{12}H_{37}ClN_9P_3$ | 33·0 | 8·5 | 8·1 | 29·0 |
| (XVII) | 33·0 | 8·7 | 8·2 | | $C_{12}H_{37}ClN_9P_3$ | 33·0 | 8·5 | 8·1 | 29·0 |
| (XVIII) | 35·9 | 9·1 | | 31·4 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XIX) | 36·2 | 8·9 | | 31·4 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XX) | 33·1 | 8·3 | 8·0 | 28·8 | $C_{12}H_{37}ClN_9P_3$ | 33·1 | 8·5 | 8·1 | 29·0 |
| (XXI) | 36·2 | 9·1 | | 31·5 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XXII) | 33·0 | 8·4 | 8·0 | 28·7 | $C_{12}H_{37}ClN_9P_3$ | 33·1 | 8·5 | 8·1 | 29·0 |
| (XXIII) | 36·0 | 9·0 | | 31·6 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XXIV) | 36·6 | 9·0 | | 31·1 | $C_{12}H_{36}N_9P_3$ | 36·1 | 9·0 | 0·0 | 31·5 |
| (XXV) | 33·0 | 8·8 | | 28·6 | $C_{12}H_{37}ClN_9P_3$ | 33·1 | 8·5 | 8·1 | 29·0 |
| (XXVI) | 36·1 | 9·0 | | 27·4 | $C_{12}H_{35}N_8OP_3$ | 36·2 | 9·0 | 0·0 | 28·0 |

invoked earlier [3] proton abstraction by amine to explain the ready formation of geminal $N_3P_3Cl_4(NHR)_2$ (R = $Bu^t$). The failure to isolate, to date, tris-geminal compounds, $N_3P_3Cl_3(NHR)_3$ (R = Et, $Pr^i$, or $Bu^t$), indicates



that the electron-supply from three substituent amino-groups to the reaction site enhances ionisation of the P–Cl bond (possibly aided by hydrogen-bonding to chlorine) to give the geminal tetrakis-compounds, $N_3P_3Cl_2(NHR)_4$ (R = Et, $Pr^i$, or $Bu^t$), and the geminal compounds, $N_3P_3Cl_2(NHR)_3(OEt)$ (R = Et or $Pr^i$). This competitive solvolysis by a weaker nucleophile (*e.g.* EtOH) also suggests that the phosphorus reaction site possesses a partial or complete positive charge when nucleophilic attack occurs. The rate of solvolysis by ethanol appears to be governed mainly by steric factors in the complexed intermediate, as the aminoethoxy-derivatives $N_3P_3Cl_2(NHR)_3(OEt)$ are formed in greatest amounts in competition with the smallest amine, $NH_2Et$. With the bulkiest amine, $NH_2Bu^t$, we failed to detect any of this type of derivative, suggesting that, if formed, its yield must be <1% of that of the tetra-amino-derivative, $N_3P_3Cl_2(NHR)_4$.

## EXPERIMENTAL

The ethylaminocyclotriphosphazatrienes were prepared by conventional methods (see, *e.g.*, refs. 2, 3, 8, 10, 24). Details of the preparations are summarised in Table 4. Yields refer to *pure* products (*i.e.* in some cases after column chromatographic separation). Analytical data are reported in Table 5.

## APPENDIX

In previous papers,[2,16,18,20,27] references to ' nongeminal $N_3P_3Cl_2(NHR)_4$ ' R = Et or $Pr^i$ should be replaced by $N_3P_3Cl_2(NHR)_3(OEt)$ R = Et or $Pr^i$ respectively. Also, the reactions of $N_3P_3Cl_2(NHPr^i)_3(OEt)$ with dimethylamine and $N_3P_3Cl_4(NMe_2)_2$ with isopropylamine, reported as giving the same product,[2] need reinvestigation.

We are indebted to B.A.S.F., Ludwigshafen, for generous gifts of chlorocyclophosphazenes.

[2/1581 *Received*, 5*th July*, 1972]

[27] S. K. Das, D. Feakins, W. A. Last, S. N. Nabi, S. K. Ray, R. A. Shaw and B. C. Smith, *J. Chem. Soc.* (*A*), 1970, 616.