Phosphorus–Nitrogen Compounds. Part XXXVII.[1] The Syntheses, Properties, and Some Reactions of (2,2,2-Triphenylphosphazen-1-yl)-cyclotriphosphazatrienes and -cyclotetraphosphazatetraenes

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Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, some of its dimethylamino-, and phenyl-derivatives, react with triphenylmonophosphazene, $HN{=}PPh_3$. The first mentioned yields a mono-($N_3P_3Cl_5{\cdot}NPPh_3$), and two non-geminal bis-triphenylphosphazenyl-derivatives, $[N_3P_3Cl_4(NPPh_3)_2]$. The others give rise to mono-substituted triphenylphosphazenyl-derivatives, the reagent attacking, where possible, at a ${\equiv}PCl_2$ grouping to give *non*geminal products to which structures are assigned. $N_3P_3Cl_5{\cdot}NPPh_3$ (*a*) reacts with 2 mol equiv. of dimethylamine to give the geminal isomer, $N_3P_3Cl_4(NMe_2)(NPPh_3)$, containing two $={PCl_2}$ groups, and (*b*) gives rise to a structurally analogous geminal ethoxy-derivative, $N_3P_3Cl_4(OEt)(NPPh_3)$, when treated with ether in the presence of various Lewis acids. $N_4P_4Cl_8$ yields with triphenylmonophosphazene, mono-$N_4P_4Cl_7{\cdot}NPPh_3$) and 2,6-di-substituted derivatives, $[N_4P_4Cl_6(NPPh_3)_2]$. The mechanisms of the above reactions are discussed in the light of the chemical and physical properties of the above and related compounds.

2,2,2-TRIPHENYLPHOSPHAZEN-1-YLCYCLOPHOSPHAZENES are defined as cyclophosphazenes, having at least one triphenylphosphazenyl group ($-N{=}PPh_3$) directly linked to a ring phosphorus atom (for nomenclature see ref. 2).

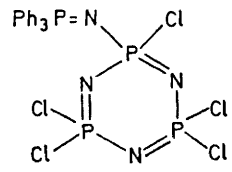
The first examples of this type, the mono-, $N_3P_3Cl_5{\cdot}NPPh_3$, (I), and the bis geminal-derivatives, $[N_3P_3Cl_4(NPPh_3)_2]$, (II), of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, were reported in 1967 [3] from this laboratory.

[1] Part XXXVI, A. P. Carroll, R. A. Shaw, and M. Woods, preceding paper.

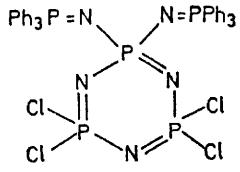
[2] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.

[3] R. Keat, M. C. Miller, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1967, 1404.

These compounds were obtained from a modified Kirsanov reaction [4] of the geminal diamino-derivative, $N_3P_3Cl_4(NH_2)_2$, and dihalogenotriphenylphosphoranes, Ph_3PX_2, (X = Cl or Br). The same compounds were



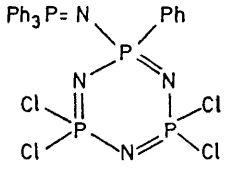
(I)



(II)

subsequently synthesised by organometallic phenylation of the 2′,2′,2′-trichloro-analogues, $N_3P_3Cl_5{\cdot}NPCl_3$, and $N_3P_3Cl_4(NPCl_3)_2$.[5] However, the lack, or relative instability, of appropriate aminocyclophosphazenes, limited the generality of these synthetic routes.

The isolation of a variety of phosphazenylcyclophosphazenes [(I), (III), and (IV)] from the organometallic phenylation [6,7] of $N_3P_3Cl_6$ or $N_4P_4Cl_8$, and Friedel–Crafts phenylation [8] [compound (III)] of $N_4P_4Cl_8$, encouraged us to investigate new synthetic routes to this type of compound.



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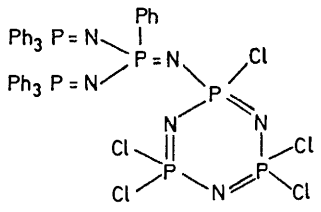


(IV)

The low electrophilic reactivity of the above phosphazenylcyclophosphazenes towards simple nucleophiles such as secondary aliphatic amines, and especially towards the more complex species present in solutions of arylmagnesium reagents,[6,7] led us to investigate the behaviour of this class of compounds in some detail.

Superficially at least, 2,2,2-triphenylphosphazen-1-ylcyclophosphazenes may be regarded as acyl-derivatives of 2,2,2-triphenylmonophosphazene (also referred to as triphenylphosphine imine), $HN{=}PPh_3$. Intensive studies over the last decade have indicated the highly reactive nature of this nucleophile ($HN{=}PPh_3$), and its preparative potential has been pointed out in recent reviews.[9]

Since chlorocyclophosphazenes are readily substituted by ' simple ' monofunctional nucleophiles, (*e.g.*, amines, alkoxides, *etc.*), we investigated the reaction of 2,2,2-triphenylmonophosphazene with chlorocyclophosphazenes as a possible route to the title compounds.

The reaction of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with 2 mol. equiv. of 2,2,2-triphenylmonophosphazene (TMP) in benzene, diethyl ether, or chloroform solution at room temperature, affords almost quantitatively the previously reported 2-(2,2,2-triphenylphosphazen-1-yl)-2,4,4,6,6-pentachlorocyclotriphosphazatriene, (I), and 1 mol. equiv. of 2,2,2-triphenylmonophosphazene hydrochloride (the by-product accompanying all the analogous reactions subsequently described). Irrespective of solvent, temperature or reaction time, provided the reactants are in the ratio of 2 : 1 (TMP : $N_3P_3Cl_6$) or less, no other products have been observed.

This behaviour contrasts sharply with the reactions of hexachlorocyclotriphosphazatriene with other nucleophiles, where either monosubstituted products are not isolated (*e.g.*, NH_3),[10] or when formed are accompanied by more highly substituted derivatives.[11] We have pointed out previously that weak nucleophiles, *e.g.*, phenolysis reagents,[11b] tend to give, even under mild conditions, products exhibiting a considerable range of degrees of replacement, whilst stronger nucleophiles [11a] give a narrower range, reflecting the greater electron-releasing capacity of the resultant substituent groups. The above observation of ' clean ' monosubstitution, suggests that the triphenylphosphazenyl-substituent possesses either extremely powerful electron-releasing properties and/or exerts considerable steric hindrance towards the approach by further TMP.

Further nucleophilic substitution by TMP is therefore expected to require rather more forcing conditions. Replacement of a second chlorine atom does indeed require prolonged treatment of the monosubstituted compound (I) with 2 (or more) mol. equiv. of TMP in refluxing benzene or chloroform.

Two products are observed under the above conditions which, although possessing almost identical chromatographic properties, are nevertheless separable by fractional crystallisation from benzene; the minor product (V), m.p. 225°, readily forms a benzene adduct, whilst the major product (VI), m.p. 230° does not. Both compounds (V) and (VI) are bis(triphenylphosphazenyl)-derivatives, and by comparison with the previously reported geminal derivative (II),[3] must be the non-geminal isomers.

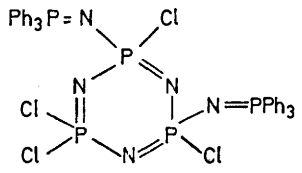
Whilst the combined yield of disubstituted isomers [(V) and (VI)] is independent of reaction solvent (provided the reaction has proceeded to completion), the proportion of the minor product (V) is slightly enhanced for reaction in chloroform compared to that in benzene (from *ca.* 5 to *ca.* 8%). However, this effect is only marginal, and to date we have been unsuccessful in converting compound (VI) into its isomer (V) by treatment in chloroform solution either with an amine hydrochloride or triphenylmonophosphazene hydrochloride,

[4] L. Horner and H. Oediger, *Annalen*, 1959, 627, 142.
[5] M. K. Feldt and T. Moeller, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2351.
[6] M. Biddlestone and R. A. Shaw, *J. Chem. Soc.* (*A*), 1970, 1750.
[7] M. Biddlestone and R. A. Shaw, *J. Chem. Soc.* (*A*), 1971, 2715.
[8] V. B. Desai, R. A. Shaw, and B. C. Smith, *Angew. Chem. Internat. Edn.*, 1968, **7**, 887.
[9] A. S. Shtepanek, E. N. Tkachenko, and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1969, **39**, 1475; M. I. Kabachnik, *Phosphorus*, 1971, **1**, 117.
[10] A. M. de Ficquelmont, *Ann. Chim.*, 1939, **12**, 169.
[11] *E.g.*, (*a*) R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215; (*b*) D. Dell, B. W. Fitzsimmons, and R. A. Shaw, *ibid.*, p. 4070.

conditions under which some (but by no means all) non-geminal aminochlorocyclotriphosphazatrienes can be converted into a mixture of *cis*- and *trans*-isomers.[12]

Treatment of compound (V) or (VI) in benzene in sealed tubes at 120° for one week with an excess of TMP affords no reaction, suggesting considerable deactivation of these molecules towards this reagent owing to polar and/or steric effects. That the latter can be of considerable importance is shown that to date we have been unable to proceed, even under very forcing conditions, beyond disubstitution, $N_3P_3Cl_4R_2$, with very bulky nucleophiles such as R = dicyclohexylamino [13] or dibenzylamino.[14]

The pK'_a values (+0·2) [15] of compounds (V) and (VI) on titration with perchloric acid in nitrobenzene solution are the same (within experimental error) and are to be compared with that of the geminal isomer (II) (+0·4).[15] The similarity of the pK'_a values of the three isomers, shows the contribution of each triphenylphosphazenyl-substituent to the overall basicity to be additive, and the site of protonation for these three isomers is almost certainly a ring nitrogen (or nitrogens) α to those phosphorus atoms carrying the greatest number of the above substituents. The slightly higher value of the geminal isomer is in keeping with prediction,[16] as two equivalent sites of protonation raise the basicity by a factor of 0·3. Protonation in some or all of the isomers on the nitrogen atom of the substituent should be mirrored by a considerable difference in pK'_a values. All other disubstituted derivatives, $N_3P_3Cl_4R_2$, of $N_3P_3Cl_6$, investigated to date, have pK'_a values well below the level of detection of our present experimental method. The above data suggest

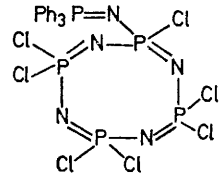


(V) and (VI)

a very high α-value (*ca.* 10·3) for the triphenylphosphazenyl-substituent. This is by far the highest α_R value so far observed in our work (*cf.* $\alpha_{NH_2} = 6{\cdot}0$, $\alpha_{NMe_2} = 5{\cdot}6$),[17] pointing to the powerful electron-releasing properties of this group at the demand of a reagent.

At present we are not in a position to ascribe unambiguously the configurations of the nongeminal isomers (V) and (VI).

Octachlorocyclotetraphosphazatetraene, when similarly treated with 2 mol. equiv. of TMP, yields as sole product the monosubstituted derivative (VII), m.p. 86—86·5°, 2-(2,2,2-triphenylphosphazen-1-yl)-2,4,4,6,6,-8,8-heptachlorocyclotetraphosphazatetraene, $N_4P_4Cl_7{\cdot}NPPh_3$, which hydrolyses slowly in moist air with evolution of hydrogen chloride. Compound (VII) reacts rather more quickly with TMP than its lower homologue (I), and reaction is essentially complete after 1 h in refluxing benzene, yielding a disubstituted derivative, $N_4P_4Cl_6(NPPh_3)_2$, (VIII), m.p. 255°, in 80% yield; another product was also detected, but not in sufficient quantity to allow its isolation. The pK'_a value (−4·6) [15] of compound (VIII) is much less than those of the disubstituted derivatives of hexachlorocyclotriphosphazatriene [(II), (V), and (VI)] and on this basis, we tentatively assign the structure as *cis*- or *trans*-2,6-bis-(2,2,2-triphenylphosphazen-1-yl)-2,4,4,6,8,8-hexachlorocyclotetraphosphazatetraene.



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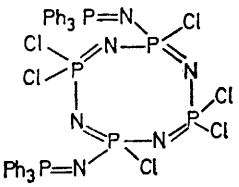
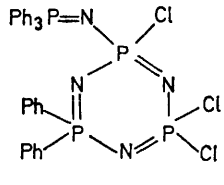


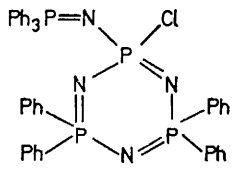
(VIII)

TMP reacts also with partially substituted chlorocyclophosphazenes (*i.e.* $N_3P_3Cl_{6-n}R_n$). The rate of reaction depends on the number (n), position, and nature of the substituents, R. Thus, mono-(2,2,2-triphenylphosphazen-1-yl)-derivatives are formed with both 2,2,4,4-tetrachloro-6,6-diphenyl- and 2,2-dichloro-4,4,6,6-tetraphenyl-cyclotriphosphazatrienes. Whereas the former yields compound (IX), $N_3P_3Ph_2Cl_3{\cdot}NPPh_3$, m.p. 186°, in refluxing benzene after only 1 h, the latter reaction requires about 24 h to go to completion under the same conditions to give (X) $N_3P_3Ph_4Cl{\cdot}NPPh_3$, m.p. 212·5°.

As expected, by far the greatest dependence upon the number and position of substituent is observed with chlorodimethylaminocyclotriphosphazatrienes. Thus pentachloromonodimethylaminocyclotriphosphazatriene, $N_3P_3Cl_5{\cdot}NMe_2$, reacts at room temperature in diethyl ether or benzene with 2 mol. equiv. of TMP to form the derivative, $N_3P_3Cl_4(NMe_2)(NPPh_3)$, (XI), m.p. 168°. The *trans*-bis-homologue, $N_3P_3Cl_4(NMe_2)_2$, however, requires a reaction time of 1 h either in boiling benzene or



(IX)



(X)

chloroform and yields a single product, $N_3P_3Cl_3(NMe_2)_2{\cdot}(NPPh_3)$, (XII), m.p. 176°. Finally, *trans*-trichlorotris-dimethylaminocyclotriphosphazatriene, $N_3P_3Cl_3(NMe_2)_3$, also gives rise to a mono-2,2,2-triphenylphosphazen-1-yl-derivative, but in this instance it is necessary to reflux the reactants in benzene for 48 h. From the reaction

[12] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 4067.
[13] S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 1961, 872.
[14] M. Hasan, R. A. Shaw, and M. Woods, unpublished results.
[15] D. Feakins, S. N. Nabi, and R. A. Shaw, unpublished results.
[16] D. Feakins, W. A. Last, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc.* (*A*), 1969, 196.
[17] D. Feakins, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc.* (*A*), 1969, 2468.

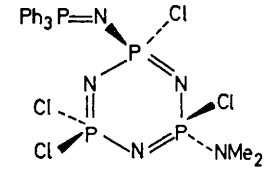
mixture compound (XIII), $N_3P_3Cl_2(NMe_2)_3(NPPh_3)$, m.p. 152°, is isolated in 80% yield.

The ^1H n.m.r. spectrum of compound (XI) shows a single methyl proton doublet of chemical shift $\tau = 7{\cdot}36$ and apparent spin–spin coupling of $^3J^*_{P-N-C-H}$ 17·0 Hz. The rather large splitting is indicative of a nongeminal $\equiv PCl{\cdot}NMe_2$ group, in line with previously reported values [18] for this grouping. This evidence suggests compound (XI) to have a nongeminal structure. The chemical shift (see Scheme) suggests a *trans*-arrangement (XI) of the two nitrogenous substituents. The ^1H n.m.r. of compound (XII) has two methyl proton doublets of equal intensity (both exhibiting long-range virtual coupling), of chemical shifts $\tau = 7{\cdot}36$ and $\tau = 7{\cdot}50$ and of equal apparent spin–spin coupling $J^*_{P-N-C-H}$ 17·0 Hz. The large spin–spin coupling indicates that the triphenylphosphazenyl-group has reacted at the $\equiv PCl_2$ group. The observation of two dimethylamino-environments shows that one must be *cis*- and the other *trans*-, with respect to the new substituent (*i.e.* the relative position of the two original substituents has remained unchanged). We assign the high and low field signals to the dimethylamino groups *cis* and *trans* respectively to the triphenylphosphazenyl group.

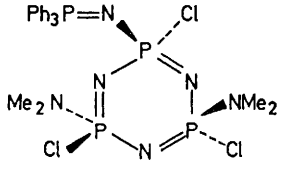
Significant up-field shifts of dimethylamino-protons in cyclotriphosphazatrienes have been observed when phenyl [19] or phenoxy [20] substituents are present, usually in a *cis*-relationship to the dimethylamino-group in question. In the present work this effect is presumably associated (i) either with a conformation which brings the dimethylamino protons under the shielding influence of the aromatic rings, and/or (ii) an electron-release by the triphenylphosphazenyl-group somewhat greater than that of dimethylamino-group. Evidence for effect (i) comes from earlier work,[19,20] for effect (ii) possibly from the generally higher chemical shifts (see Scheme) of the compounds discussed here with structurally related chlorodimethylamino-analogues, although this too could be attributed, at least in part, to effect (i). The propeller-shaped arrangement of the phenyl rings of the $Ph_3P{=}N-$ group [21] gives more opportunity than simple phenyl or phenoxy substituents, for effect (i) to be operative in different parts of the molecule. A further discussion of this must be deferred until the detailed geometry of molecules of this type has been investigated. *X*-Ray crystallographic studies to this end are in progress.

Finally, the ^1H n.m.r. spectrum of compound (XIII) shows two methyl proton doublets in the intensity ratio of 2 : 1 and of chemical shift and apparent spin-spin coupling $\tau = 7{\cdot}41$, $J^*_{P-N-C-H}$ 17·0 Hz; and $\tau = 7{\cdot}52$, $J^*_{P-N-C-H}$ 13·6 Hz respectively. The former signal shows the hump characteristic of long-range virtual coupling; its large coupling constant indicates a non-geminal structure $\equiv PCl{\cdot}NMe_2$. As with this J^*-value, only a single environment is observed, two dimethylamino-groups are probably equivalent. We thus need to consider only structures (XIIIA and B). The low chemical shift suggests that the two equivalent dimethylamino-groups are *trans*- to the 2,2,2-triphenylphosphazen-1-yl-substituent (XIIIB). The chemical shift and coupling constant of the remaining dimethylamino-group resembles closely the parameters of the dimethylamino-group geminal to the triphenylphosphazenyl-substituent in compound (XIV). We thus favour structure (XIIIB) over (XIIIA), which implies inversion of configuration at the unique dimethylamino-group in the starting material. This result would be predicted from the *cis*-effect [22] and indeed all the structures (XI), (XII), and (XIIIB), where geometric isomerism is possible, are consistent with this effect.

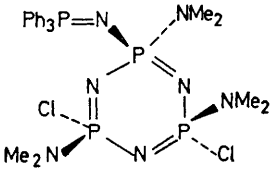
Replacement of the remaining chlorine atoms in compounds (XI), (XII), and (XIII) with dimethylamine at



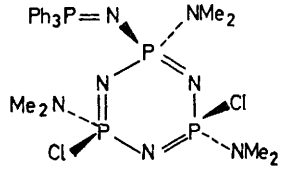
(XI)



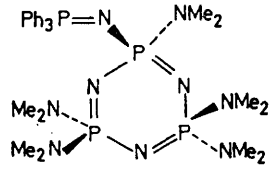
(XII)



(XIIIA)



(XIIIB)



(XIV)

elevated temperatures in the presence of triethylamine yields the previously reported [3] pentakisdimethylamino-derivative (XIV), $N_3P_3(NMe_2)_5(NPPh_3)$, m.p. 153°. The ^1H n.m.r. spectrum of compound (XIV) shows three methyl proton doublets in the intensity ratio of 2 : 2 : 1 ($\tau = 7{\cdot}38$, $J^*_{P-N-C-H}$ 11·0 Hz; $\tau = 7{\cdot}58$, $J^*_{P-N-C-H}$ 11·2 Hz; $\tau = 7{\cdot}51$, $J^*_{P-N-C-H}$ 12·9 Hz). The first two of these show long-range virtual coupling; the third doublet does not, but is rather broadened.

These observations are consistent with reactions between TMP and chlorocyclophosphazenes taking place

[18] *E.g.*, R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 1965, 7193.

[19] B. Grushkin, M. G. Sanchez, M. V. Ernest, J. L. McClanahan, G. E. Ashby, and R. G. Rice, *Inorg. Chem.*, 1965, **4**, 1538.

[20] D. Dell, B. W. Fitzsimmons, R. Keat, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1680.

[21] A. F. Cameron, N. J. Haine, and D. G. Morris, *Chem. Comm.*, 1971, 918.

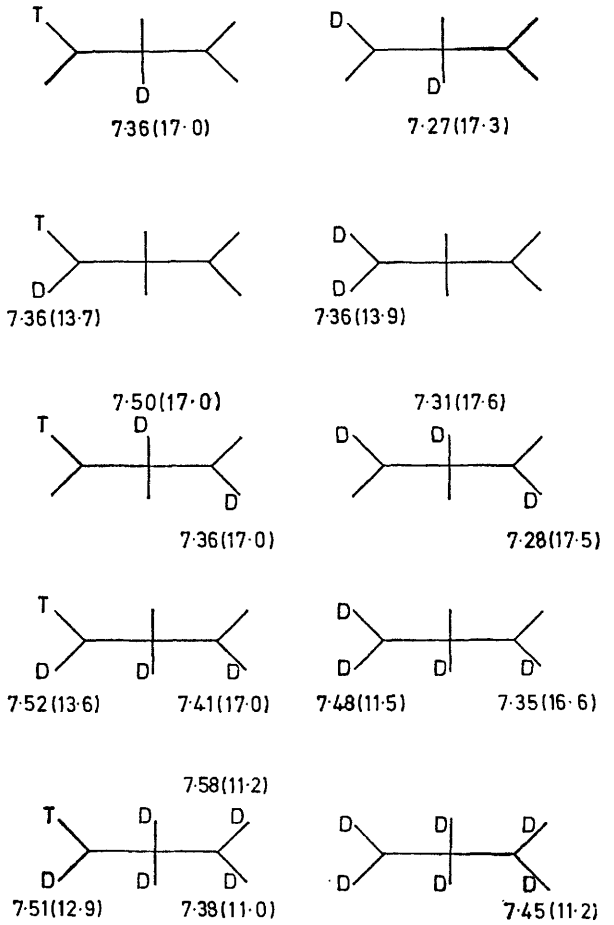
[22] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 908.

either by an S_N2 type mechanism, or by a 5-co-ordinate intermediate, the position of substitution being always the point of lowest electron-density. The very marked difference in the rate of substitution by a second triphenylphosphazenyl-group compared to that by the first, suggests that the 2,2,2-triphenylphosphazen-1-ylcyclophosphazene (I) is strongly deactivated towards further substitution by TMP, either due to a strong electron-releasing power of the phosphazenyl group, or by its steric effect (see above). The former should favour heterolysis of the phosphorus–chlorine bond, either by an S_N1-type mechanism or by one involving electrophilic attack on chlorine. For both of these, the effect should be most enhanced in the case of a phosphorus–chlorine bond located geminal to a triphenylphosphazen-1′-yl-substituent. Nucleophiles could therefore react either by an S_N2-type mechanism, which would probably take place nongeminal with respect to a triphenylphosphazenyl-substituent (*e.g.* another TMP molecule) or by an ionisation type of mechanism (S_N1 or nucleophilic attack at phosphorus assisted by an acceptor molecule interacting with the chlorine atom), which would preferentially lead to the geminal isomer.

When compound (I) is treated at room temperature with 2 mol. equiv. of dimethylamine in diethyl ether or benzene, a monodimethylamino-derivative, $N_3P_3Cl_4(NMe_2)(NPPh_3)$, (XV), m.p. 205, is formed and no trace of the other isomer (XI), (or of any other derivative) could be detected.

The ^1H n.m.r. spectra of the isomer (XV) shows a single methyl proton doublet at $\tau = 7{\cdot}35$, $J^*_{P-N-C-H}$ 13·7 Hz. The relatively low value of the coupling constant indicates that compound (XV) is 2,2,4,4-tetrachloro-6-dimethylamino-6-(2,2,2-triphenylphosphazen-1-yl)cyclotriphosphazatriene.

The structural assignments for the triphenylphosphazenyl-derivatives of chlorodimethylaminocyclotriphosphazatrienes become particularly persuasive by comparison of chemical shifts and apparent spin–spin coupling constants of structurally related dimethylamino-compounds containing a dimethylamino-group (D) in place of the triphenylphosphazenyl-group (T) as shown in the Scheme. The chlorodimethylaminocyclotriphosphazatrienes were studied in carbon tetrachloride solution; the present series of compounds in deuteriochloroform solution (low solubility in carbon tetrachloride). In the former series, chemical shifts varied for the groupings $\equiv PCl{\cdot}NMe_2$ and $\equiv P(NMe_2)_2$ by 0·10 (τ = 7·25—7·35) and 0·12 p.p.m. (τ = 7·36—7·48) respectively. In the latter (more limited) series chemical shift variations for the structural units $\equiv P(NMe_2)(NPPh_3)$, $\equiv PX{\cdot}NMe_2$ (X = Cl or NMe_2) ($-NMe_2$ *trans*- to $-NPPh_3$), and $\equiv PX{\cdot}NMe_2$ (X = Cl or NMe_2) ($-NMe_2$ *cis*- to $-NPPh_3$) of 0·16 (τ = 7·36—7·52), 0·05 (τ = 7·36—7·41), and 0·08 p.p.m. (τ = 7·50—7·58), respectively were observed. It can be seen that in the triphenylphosphazenyl-derivatives, comparable groups give, in general, signals at somewhat higher fields than in the related dimethylamino-derivatives. Coupling constants are closely related in the two series and occur in the range 16·6—17·6 Hz for $\equiv PCl{\cdot}NMe_2$ and 11·0—13·9 Hz for $\equiv P(NMe_2)_2$ or $\equiv P(NMe_2)(NPPh_3)$.

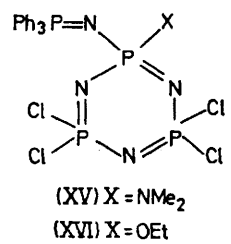


A comparison of chemical shifts and of apparent spin-spin coupling constants for related triphenyl phosphazenyl- and dimethylamino-cyclotriphosphazatrienes

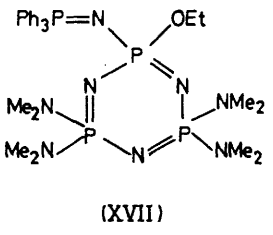
SCHEME [a,b]

[a] τ-values of NMe_2 groups with $J^*_{P-N-C-H}$ in brackets. [b] T = $NPPh_3$, D = NMe_2, no symbol indicates Cl

It has earlier been reported that compound (I) does not phenylate with phenylmagnesium bromide in diethyl ether.[6] This has been confirmed in the present work, but



(XV) X = NMe_2
(XVI) X = OEt



(XVII)

very slow reaction to give an ethoxy-derivative of (I) has been observed. Elemental analysis and ^1H n.m.r. spectroscopy show that the product (XVI), m.p. 152°, is a mono-ethoxy compound, $N_3P_3Cl_4(OEt)(NPPh_3)$ (τ_{CH_3} = 8·75, $J_{H-C-C-H}$ 7·2 Hz; τ_{CH_2} = 6·09). This

ethoxy-derivative, (XVI), is also obtained when compound (I) is treated in diethyl ether with ferric chloride, stannic chloride, or anhydrous magnesium bromide.

When compound (XVI) is treated with an excess of dimethylamine all remaining chlorine atoms are replaced by amino-residues to give compound (XVII), $N_3P_3(NMe_2)_4(OEt)(NPPh_3)$, m.p. 131°. The ^1H n.m.r. spectrum of this compound shows two dimethylamino proton doublets of equal intensity (exhibiting long-range virtual coupling) and of chemical shifts $\tau = 7{\cdot}56$ and 7·41 and apparent spin–spin couplings $J^*_{P-N-C-H}$ 11·0 Hz and $J^*_{P-N-C-H}$ 11·1 Hz, respectively, which proves conclusively that the ethoxy-group ($\tau_{CH_3} = 8{\cdot}95$, $J_{H-C-C-H}$ 7·2 Hz; $\tau_{CH_2} = 6{\cdot}17$, $J^*_{P-O-C-H}$ 9·2 Hz) is geminal with respect to the triphenylphosphazenyl-substituent in compounds (XVII) and hence also (XVI).

We have shown [3] earlier that compound (I), $N_3P_3Cl_5{\cdot}NPPh_3$, is slowly converted by benzene in the presence of aluminium chloride into the geminal phenyl derivative (III), $N_3P_3PhCl_4(NPPh_3)$. Hence, all reactions of compound (I), studied to date, except that with further TMP (where steric hindrance may play a part) occur with replacement of the chlorine atom geminal to the triphenylphosphazenyl group.

In trying to rationalise the properties and reactions of triphenylphosphazenylcyclotriphosphazatrienes, which differ considerably from those of previously reported cyclotriphosphazatrienes, we must distinguish between the properties of the molecules in their ground state and those when the molecules become perturbed at the demand of a reagent. We have demonstrated recently an approximately linear relationship between phosphorus–chlorine bond-length and ^{35}Cl n.q.r. coupling constant.[23] We suggested that the longer bonds and the lower coupling constants were associated with greater ionic character of the P–Cl bonds.[23] The ^{35}Cl n.q.r. spectrum of compound (I) (for which we are greatly indebted to Professor J. A. S. Smith and Dr. G. Jugie of Queen Elizabeth College) shows the following absorptions at liquid-nitrogen temperature (room temperature values in brackets): $25{\cdot}12_0$ ($24{\cdot}57_2$); $27{\cdot}81_0$ ($27{\cdot}09_5$); $27{\cdot}63_6$ ($26{\cdot}90_6$, $26{\cdot}99_4$); $27{\cdot}46_2$ ($26{\cdot}66_2$) MHz. The coupling constants for nongeminal $\equiv PCl{\cdot}NPPh_3$ and geminal $\equiv PCl_2$ chlorine atoms are very similar to those for corresponding dialkylamino-derivatives.[24]

If the above quoted relationship holds also for the TMP-derivatives, the P–Cl bond length and ionic bond character in the moieties $\equiv PCl{\cdot}NAlk_2$ and $\equiv PCl{\cdot}NPPh_3$, should be about the same.

The chemical shifts of the dimethylamino-protons in TMP-derivatives occur at somewhat higher field than in the corresponding dimethylamino-derivatives (see Scheme). This could be due to a somewhat greater electron-supply by the TMP than by the NMe_2 group and/or magnetic shielding. *X*-Ray crystallographic investigations should throw light on this. The ground-state properties cited above hardly explain the extraordinary behaviour of TMP-derivatives.

The difficulty experienced in introducing more than two TMP groups into the cyclotriphosphazatriene molecule is, in the light of the experience gained with other bulky substituents (*e.g.*, dibenzylamino [14] and dicyclohexylamino,[13]) probably largely steric in origin. Hence in this respect, the TMP groups are not exceptional. However, the extraordinary high basicities which the TMP groups (compared to those of other substituent groups so far investigated) induce in cyclotriphosphazatriene-derivatives, renders these groups unique. We have shown earlier that the substituent constants α_R decreased in the series $R = NH_2 > NHMe > NMe_2$ [17] and $NHEt > NMe_2$.[17] Since the order of this series is the reverse of that expected if inductive effects alone were operating, it is thought that steric effects must be involved. We assume that the smaller groups can assume more readily than the larger ones, conformations which favour electron-supply to the ring, if the reagent demands so. The nitrogen atom of the TMP-substituent is only 2-co-ordinate and hence has more possibilities for fulfilling an electron-supplying role. In the alkoxyphosphazenes, *e.g.* $N_3P_3(OR)_6$, the 2-co-ordinate oxygen atom, has a similar freedom to supply electrons, and hence basicities increase with the inductive effect of the groups $R = Me < Et < Pr^i$.[25]

In the light of the above, we can hardly invoke an S_N1-mechanism to explain the formation of compounds (III), (XV), and (XVI) from compound (I). It seems likely that either electrophilic attack on chlorine or nucleophilic attack at phosphorus assisted by polarisation of the P–Cl bond by electrophilic reagents, would rationalise the above product formation. In the phenylation and ethoxylation Lewis acids (*e.g.* $AlCl_3$, $FeCl_3$, $SnCl_4$, PhMgBr), are present: in the aminolysis hydrogen-bonding of the amine to the chlorine atom may facilitate its departure as a chloride ion. It is possible that the presence of Lewis and Brønsted acids in the vicinity of the reaction site is favoured by the donor properties of the exocyclic phosphazenyl nitrogen atom.

The above mechanistic hypotheses are supported by chemical and physical evidence from related compounds. We have already quoted data from ^{35}Cl n.q.r. spectroscopy.[24] Phenylation of cyclotriphosphazatriene derivatives by benzene in the presence of aluminium chloride takes place exclusively at $\equiv PCl{\cdot}NR_2$ (R = Alk) groups (to give $\equiv PPh{\cdot}NR_2$) [26,27] before any $\equiv PCl_2$ groups present (to give $\equiv PPh_2$) are attacked). (Note that under those conditions $\equiv PClPh$ groups have not been detected.[28])

Very accurate *X*-ray crystallographic determinations

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have shown that in both cyclotriphosphazatriene [29,30] and cyclotetraphosphazatetraene derivatives,[31–34] the phosphorus–chlorine bonds are significantly longer in the nongeminal ≡PCl·NMe_2 and ≡PClPh groups, than in the geminal ≡PCl_2 structural units.[29,34–37] This increase in bond-length undoubtedly reflects a greater degree of ionic character and this, in turn, rationalises those reactions carried out in the presence of Lewis acids.

We have shown elsewhere that when two different amino-residues are introduced into a cyclotriphosphazatriene, that it is the nucleophile rather than the substituent which determines the structure of the product,[38–40] and have recently suggested a rationalisation for this.[41] Whilst two dimethylamino [11a] or two TMP-residues give rise to nongeminal structures, and the mixed derivative (XI) has also the anticipated nongeminal structure, compound (XV) appears an exception to the above rule. The anomaly may have its origin in the potential donor capacity of the nitrogen atom of the TMP-substituent.

The observations made in the present study suggest that we may have to make a distinction between two types of steric effects: (*a*) those which may prevent or hinder the approach of a reagent, and (*b*) those which determine the conformation a particular substituent group can take up to supply electrons at the demand of a reagent. These two effects need not always act in the same direction, *e.g.* a group which may be prevented from attacking a given reaction site, need not, if introduced by an indirect method, interfere with the other substituent, already present, taking up a conformation favourable to supply electrons.

EXPERIMENTAL

Benzene, diethyl ether, and light petroleum (b.p. 60—80°) were distilled from sodium hydride and stored over molecular sieve type 3A. Chloroform was dried by contact with active granular alumina and decanted prior to use. 2,2,2-Triphenylmonophosphazene (TMP) was obtained from Maybridge Chemical Co., Tintagel, U.K. The cyclophosphazene-derivatives were synthesised by methods described in the literature from hexachlorocyclotriphosphazatriene.[11,28]

Preparation of 2,2,2-Triphenylphosphazen-1-yl Derivatives.—The chloro-precursor (0·01 mol) was dissolved in benzene (30 ml) and mixed with a solution of TMP [0·02 mol (or more; see text)] in benzene (50 ml). The mixture was shaken and set aside, or refluxed according to the requirements of the reaction, which was always carried out under an atmosphere of nitrogen.

After completion of the reaction (as observed by no further precipitation taking place) the TMP hydrochloride was filtered off, washed with diethyl ether, dried, and weighed (to check completion of reaction). The filtrate was concentrated to small bulk and light petroleum added. On cooling the product crystallised.

2,2,4,4-Tetrachloro-6-dimethylamino-6-(2,2,2-triphenyl phosphazen-1-yl)cyclotriphosphazatriene (XV).—A solution of compound (I) (5·2 g, 0·01 mol) in diethyl ether (100 ml) was treated dropwise with stirring with dimethylamine (0·9 g, 0·02 mol) in diethyl ether (25 ml). After addition, the mixture was heated under reflux (10 min), dimethylamine hydrochloride was filtered off, and then light petroleum was added to the concentrated filtrate. Upon cooling *2,2,4,4-tetrachloro-6-dimethylamino-6-(2,2,2-triphenylphosphazen-1-yl)cyclotriphosphazatriene* (XV), m.p. 205° (sublimes), 5 g, 90%) crystallised. (Found: C, 40·1; H, 3·3; N, 12·0; P, 20·7. $C_{20}H_{21}Cl_4N_5P_4$ requires C, 40·2; H, 3·5; N, 11·7; P, 20·8%).

Reaction conditions for synthesis and yields and elemental analyses for triphenylphosphazenylcyclophosphazenes

Chlorocyclophosphazene precursor	Solvent	*t*/°C	Time h	Product	Found (%) C	H	Cl	N	P	Formula	Requires (%) C	H	Cl	N	P	Yield (%)	Product m.p.(*t*/°C
$N_3P_3Cl_6$	PhH, Et_2O $CHCl_3$*	25	1/6	$N_3P_3Cl_5(NPPh_3)$ (I)	36·7	2·8	30·0	9·5	20·8	$C_{18}H_{15}Cl_5N_4P_4$	36·7	2·6	30·2	9·5	21·0	95	215°
(I) $N_3P_3Cl_5(NPPh_3$	PhH†	81	30	$N_3P_3Cl_4(NPPh_3)_2$·PhH (V)	55·5	4·0	15·4	7·8	17·0	$C_{42}H_{36}Cl_4N_5P_5$	55·5	4·0	15·7	7·7	17·1	5	225
				$N_3P_3Cl_4(NPPh_3)_2$ (VI)	51·9	3·7	17·0	8·6	18·6	$C_{36}H_{30}Cl_4N_5P_5$	52·1	3·6	17·1	8·4	18·7	85	230
	$CHCl_3$*†	61	24	$N_3P_3Cl_4(NPPh_3)_2$·PhH (V)												8	225
				$N_3P_3Cl_4(NPPh_3)_2$ (VI)												85	230
$N_4P_4Cl_8$	PhH	25	1/6	$N_4P_4Cl_7(NPPh_3)$ (VII)	30·8	2·1	35·2	10·1	22·2	$C_{18}H_{15}Cl_7N_5P_5$	30·7	2·2	35·3	10·0	22·0	80	86—86·6
(VII) $N_4P_4Cl_7(NPPh_3$	PhH	81	4	$N_4P_4Cl_6(NPPh_3)_2$ (VIII)	46·0	3·5	22·8	8·8	19·5	$C_{36}H_{30}Cl_6N_6P_6$	45·7	3·2	22·5	8·9	19·7	80	255
gem-$N_3P_3Ph_2Cl_4$	PhH	81	1	$N_3P_3Ph_2Cl_3(NPPh_3)$ (IX)	53·9	3·7	15·8	8·1	18·7	$C_{30}H_{25}Cl_3N_4P_4$	53·6	3·8	15·9	8·3	18·5	85	186
gem-$N_3P_3Ph_4Cl_2$	PhH	81	24	$N_3P_3Ph_4Cl(NPPh_3)$ (X)	66·5	4·8	4·8	7·6	16·5	$C_{42}H_{35}Cl\,N_4P_4$	66·7	4·7	4·7	7·4	16·5	80	212·5
$N_3P_3Cl_5(NMe_2)$	PhH, Et_2O	25	1/6	$N_3P_3Cl_4(NMe_2)(NPPh_3)$ (XI)	40·0	3·3	23·8	12·3		$C_{20}H_{21}Cl_4N_5P_4$	40·2	3·5	23·8	11·7		95	168
trans-$N_3P_3Cl_4(NMe_2)_2$	PhH, $CHCl_3$	81 61	1 1	$N_3P_3Cl_3(NMe_2)_2(NPPh_3)$ (XII)	44·3	4·7	17·2	13·8	19·8	$C_{22}H_{27}Cl_3N_6P_4$	43·6	4·5	17·5	13·9	20·5	80	176
trans-$N_3P_3Cl_3(NMe_2)_3$	PhH	81	48	$N_3P_3Cl_2(NMe_2)_3(NPPh_3)$ (XIII)	46·5	5·5	11·4	15·7		$C_{24}H_{33}Cl_2N_7P_4$	46·9	5·4	11·6	15·9		80	152

* After reaction the solvent was removed *in vacuo* and the residue extracted with benzene. The insoluble matter comprised TMP hydrochloride. † Reaction products crystallized from benzene. 80% of (VI) crystallizes from dilute benzene solution. The benzene adduct (V) stays in solution until nearly all of (VI) has crystallized out.

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2,2,4,4-*Tetrachloro*-6-*ethoxy*-6-(2,2,2-*triphenylphosphazen*-1-*yl*)*cyclotriphosphazatriene* (XVI).—A solution of compound (I) (5·2 g, 0·01 mol) in diethyl ether (100 ml) was treated with a solution of magnesium bromide in diethyl ether (from 0·5 g Mg and 3·6 g of ethylene dibromide in 50 ml of diethyl ether) and the mixture was heated under reflux (48 h). The solution was cooled, extracted with ice-cold aqueous ammonium chloride, the ether layer dried (Na_2SO_4), the solvent evaporated, and the residue recrystallised from light petroleum (b.p. 60—80°) to give 2,2,4,4-*tetrachloro*-6-*ethoxy*-6-(2,2,2-*triphenylphosphazen*-1-*yl*(*cyclotriphosphazatriene* (XVI), m.p. 152° (3·6 g, 60%). (Found: C, 40·3; H, 3·3; N, 9·5; P, 20·6. $C_{20}H_{20}Cl_4N_4OP_4$ requires C, 40·2; H, 3·3; N, 9·4; P, 20·7%).

Dimethylaminolysis of Products.—The partially substituted phosphazenes were heated with a five-fold excess (for complete aminolysis) of dimethylamine in benzene in a sealed tube at 150° overnight. The amine hydrochloride was filtered off, the solvent was evaporated from the filtrate, and the derivative recrystallised from light petroleum.

All reaction mixtures were investigated by t.l.c. on alumina to check the absence of other products besides those reported here. N.m.r. spectra were obtained at 60 MHz on a Varian A60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as internal reference standard. The ^{35}Cl n.q.r. spectra were recorded on a Decca n.q.r. spectrometer with side-band suppression.

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