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CYCLOPHOSPHAZENES—INORGANIC HETEROCYCLIC COMPOUNDS WITH ORGANIC TYPE REACTIVITY*

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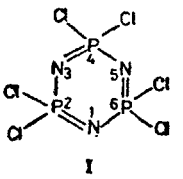
The different types of reactions undergone by cyclophosphazenes and the complex nature of bonding present in these compounds set them apart from other phosphorus-nitrogen compounds or indeed from other inorganic heterocyclic systems. Recent findings on the aminolysis reaction of chlorocyclotetraphosphazenes to yield both (amino) cyclotetraphosphazenes and novel *trans*-annular bridged bicyclic phosphazenes, the reactions of chlorocyclophosphazenes with difunctional reagents, nucleophilic substitution reactions of triphenylphosphazenyl derivatives, $N_3P_3X_5(NPPh_3)$ (X = F, Cl) and synthesis and thermal rearrangement of (alkoxy) (aryloxy) cyclotriphosphazenes are reviewed. A unified mechanistic framework has emerged for nucleophilic displacement reactions of halogenocyclophosphazenes from kinetic studies on selected systems and this aspect is highlighted. Structural features as revealed by X-ray diffraction and NMR spectroscopy and new approaches for phosphazene polymers are also briefly discussed.

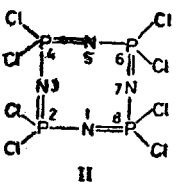
Key Words : Cyclotri-, Cyclotetra- and Bicyclic Phosphazenes; Reaction Mechanisms; Phosphorus-Nitrogen Polymers

INTRODUCTION

ALTHOUGH the first inorganic heterocyclic compound, $N_3P_3Cl_6$(I), was reported as for back as 1834 by Leibig and Wohler and its cyclic nature as well as that of its higher homologue (II) recognised by Stokes in 1895–6, systematic studies of the chemistry of such systems began to take deep roots only in the later half of this century.[1–4] Seldom among inorganic heterocyclic systems, one encounters an homologous series of compounds as extensive as that found for cyclophosphazenes; compounds containing upto eight (NPX_2) units in the ring have been well



I



II

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characterised. Cyclophosphazenes resemble organic systems very much in their reactivity, the ring skeleton persists through several reaction sequences. Some typical reactions[1,3,5–7] of $N_3P_3Cl_6$(I) are illustrated in Fig. 1.

The interest in cyclophosphazenes had been primarily stimulated by the intriguing nature of bonding between phosphorus and nitrogen in these formally valence unsaturated systems which to this day continues to be a challenge to the theoreticians[8,9]. In recent years, the prospect of technological applications of cyclophosphazenes in diverse fields[3,10,11] as well as the successful synthesis and characterisation of many linear polyphosphazenes[1,12–14] has provided a great impetus for the rapid development of the chemistry of the cyclic systems, which may be viewed as "models" for macromolecular synthesis.[15]

We have carried out extensive investigations on cyclophosphazenes with particular emphasis on the eight-membered ring system represented by II, which in view of its greater skeletal flexibility, is a better "model" for the reactions of polymers than its more rigid six-membered homologue(I). Our studies span a wide range and encompass synthetic, spectroscopic, structural and mechanistic aspects.[16] A novel P_4N_5 bicyclic system has been uncovered (in a serendipitous manner) and the mechanism of its formation by an intramolecular nucleophilic substitution reaction has been elucidated. New insights into the mechanisms of nucleophilic substitution reactions of halogenocyclophosphazenes have emerged as a result of synthetic and kinetic studies on carefully chosen systems and the results enable us to formulate a unified mechanistic framework to explain the "regio and stereo selectivity" observed for this class of reactions. The signifieant highlights of these investigations are presented in this review.

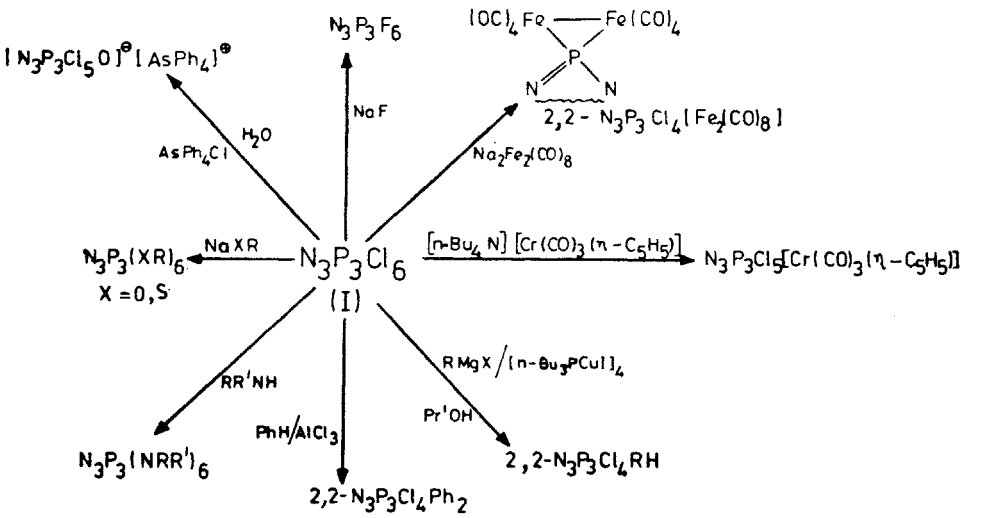
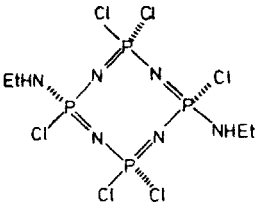


FIG. 1 Typical reaction of $N_3P_3Cl_6$(I)

Aminolysis Reactions of Chlorocyclotetraphosphazenes—Formation of Novel Bicyclic Phosphazenes

The first bicyclic phosphazene, $N_4P_4(NMe_2)_5$ (NHEt) (NEt) (VI, $R = R'$ Et) was isolated in our laboratory by Sau from the reaction of 2-*trans*-6-$N_4P_4Cl_6(NHEt)_2$ (III) with an excess of dimethylamine in chloroform.[17,18] The choice of solvent was unintentional. Subsequently, when the reaction was carried out in diethyl



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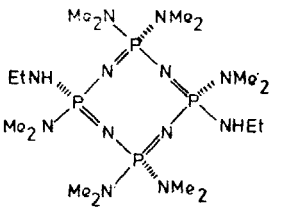
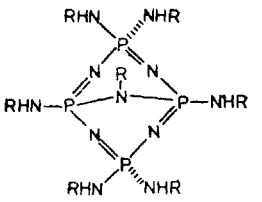
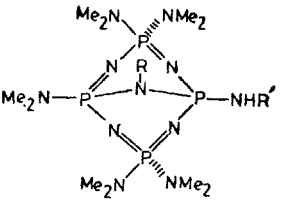


IV



V



VI

R = Me, Et, Pr^n, Pr^i, Bu^n

R = R' = Me, Et, Pr^n, Bu^n, CH_2Bu^t, CH_2Ph

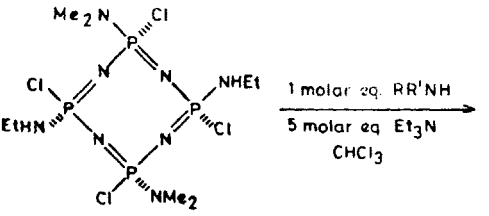
R = Et, R' = Bu^t

ether, only the fully aminolysed cyclotetraphosphazene(IV) was obtained. Further studies have revealed that the aminolysis reactions of $N_4P_4Cl_8$(II) or its primary amino derivatives can proceed in three ways : (i) "normal" stepwise replacement of chlorine atoms to give chloro(amino) and octakis(amino) cyclotetraphosphazenes, (ii) intramolecular nucleophilic attack leading to the formation of novel bicyclic phosphazenes and (iii) intermolecular condensation resulting in crosslinked products. The competition among these three processes depends on the substituent present on the phosphazene ring, the nucleophile and (to a very significant extent) the nature of the reaction medium. Chloroform or dichloromethane promotes the formation of bicyclic derivative; in diethyl ether or CCl_4 the yield of bicyclic phosphazene (if at all formed) is very low (< 5 per cent). Methyl cyanide shows an intermediate behaviour.[19]

Symmetrically substituted bicyclic phosphazenes of type, $N_4P_4(NHR)$ (NR) (V) are formed when $N_4P_4Cl_8$(II) reacts with an excess of a primary amine in chloroform.[18,20,21] Asymmetrically substituted bicyclic phosphazenes of type, $N_4P_4(NMe_2)_5$ (NH*R'*) (N*R*) (VI) can be prepared from the reaction of 2,6-$N_4P_4Cl_6$

(NH*R*) (NH*R'*) with an excess of dimethylamine in chloroform.[18,19,22] The relative yield of the bicyclic phosphazene increases in the order $R = R' = CH_2Bu^t < Bu^n < Me < CH_2Ph < Et < Pr^n$. Bicyclic phosphazenes are not formed when the primary amino substituent is α-branched (e.g. $R = R' = Pr^i$, Bu^t, Ph).

We have recently shown that the formation of bicyclic phosphazene from $N_4P_4Cl_8$ occurs only after the tetrakis stage of chlorine replacement. The tetrakis (amino) derivative, $N_4P_4Cl_4(NHEt)_2$ $(NHEt)_2$ $(NMe_2)_2$ (VII) has been isolated and its versatility for the preparation of bicyclic phosphazenes containing different amino substitutents(VIII) have been established.[23] The reaction 2,4,6,8-$N_4P_4Cl_4$ $(NHEt)_4$ (IX) with dimethylamine affords the bicyclic phosphazene, $N_4P_4(NHEt)_3$ $(NMe_2)_3$ (NEt) (X). The reactions of 2-*trans*-6-$N_4P_4Cl_6(NMePh)_2$, 2-*trans*-4-$N_4P_4Cl_6(NMePh)_2$, 2,6-$N_4P_4Cl_6(NHBu^t)_2$ 2,4-$N_4P_4Cl_6(NHBu^t)_2$, 2,6-$N_4P_4Cl_6$ $[N(CH_2Ph)_2]_2$ with ethylamine in chloroform in the presence of triethylamine have also been studied and the results bring out the subtle aspects of the mechanism of formation of bicyclic phosphazene.[22] Formation of *trans*-annular bridge occurs only when the cyclophosphazene substrate bears primary amino substituents (NHR) at the antipodal phosphorus atoms and at least one of the *R* groups is capable of being accommodated at the bridgehead nitrogen. The bridging of adjacent phosphorus atoms by an N*R* group does not take place under any circumstances. A base assisted proton abstraction step generates a three-coordinated P^V intermediate (XI) (for evidence of such a species in cyclophosphazenes, see Section G).



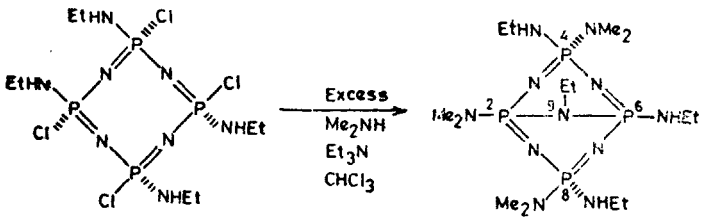
VII

VIII

R = Me , R' = Me

R = Et , R' = H

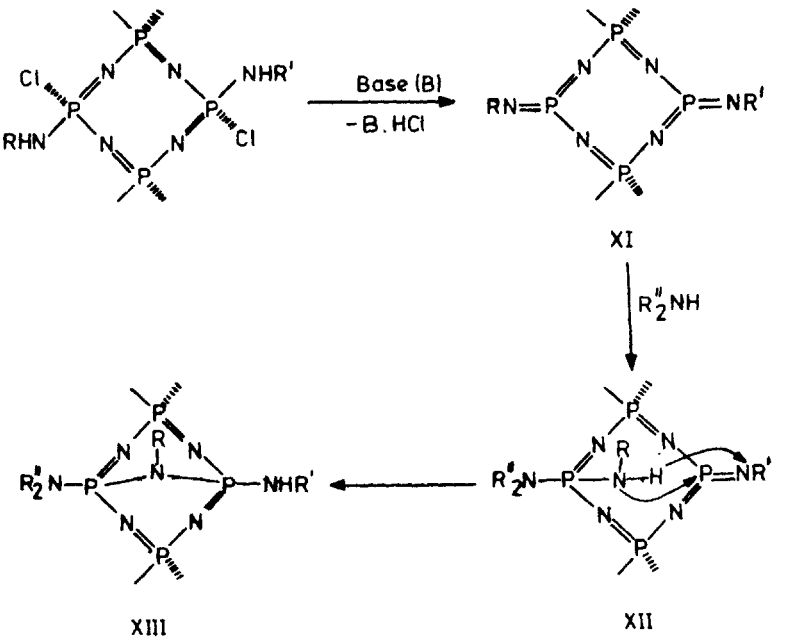
RR' = C_4H_8O (morpholino)



IX

X

Intramolecular addition of an NH*R* group from the antipodal phosphorus to the exocyclic phosphorus-nitrogen double bond would afford the bicyclic phosphazene(XIII).



Bicyclic phosphazenes can be readily distinguished from the corresponding fully aminolysed cyclotetraphosphazenes by IR and ^{31}P NMR spectroscopy. The ^{31}P chemical shifts of the former (15–25δ) lie $\sim$ 10 ppm downfield as compared to the chemical shifts of the later (4–12δ). The ^{31}P NMR technique is thus very useful for determining the relative yields of the two types of products particularly in those instances where the bicyclic phosphazenes cannot be separated from the reaction mixture.[18–24] A typical spectrum is shown in Fig. 2.

It is essential to record the proton NMR spectra of bicyclic phosphazenes at high fields (> 5 Tesla) in order to make a complete analysis of the spectrum and assign the various resonances.[19-21] The spectrum of the bicyclic compound, $N_4P_4(NMe_2)_5$ (NHEt) (NEt) at 270MHz is shown in Fig 3 along with the assignments. The data confirm the bicyclic structure. The protons of the groups attached to the junction phosphorus atoms [P(2),P(6)], are considerably deshielded and this deshielding extends even to the γ-protons.[19,21] The two NMe_2 substituents at P(4) or P(8) are nonequivalent. An analysis of the shifts observed on the addition of Eu(fod)$_3$ indicates that the protons of the NMe_2 group pointing to the bridgehead nitrogen atom resonates at a higher field.[18]

X-ray crystallographic studies of the bicyclic phosphazenes, $N_4P_4(NMe_2)_5$ (NHEt) (NEt),[25] $N_4P_4(NHMe)_6$ (NMe)[26] and $N_4P_4(NMe_2)_5$ (NHMe) (NMe)[27]

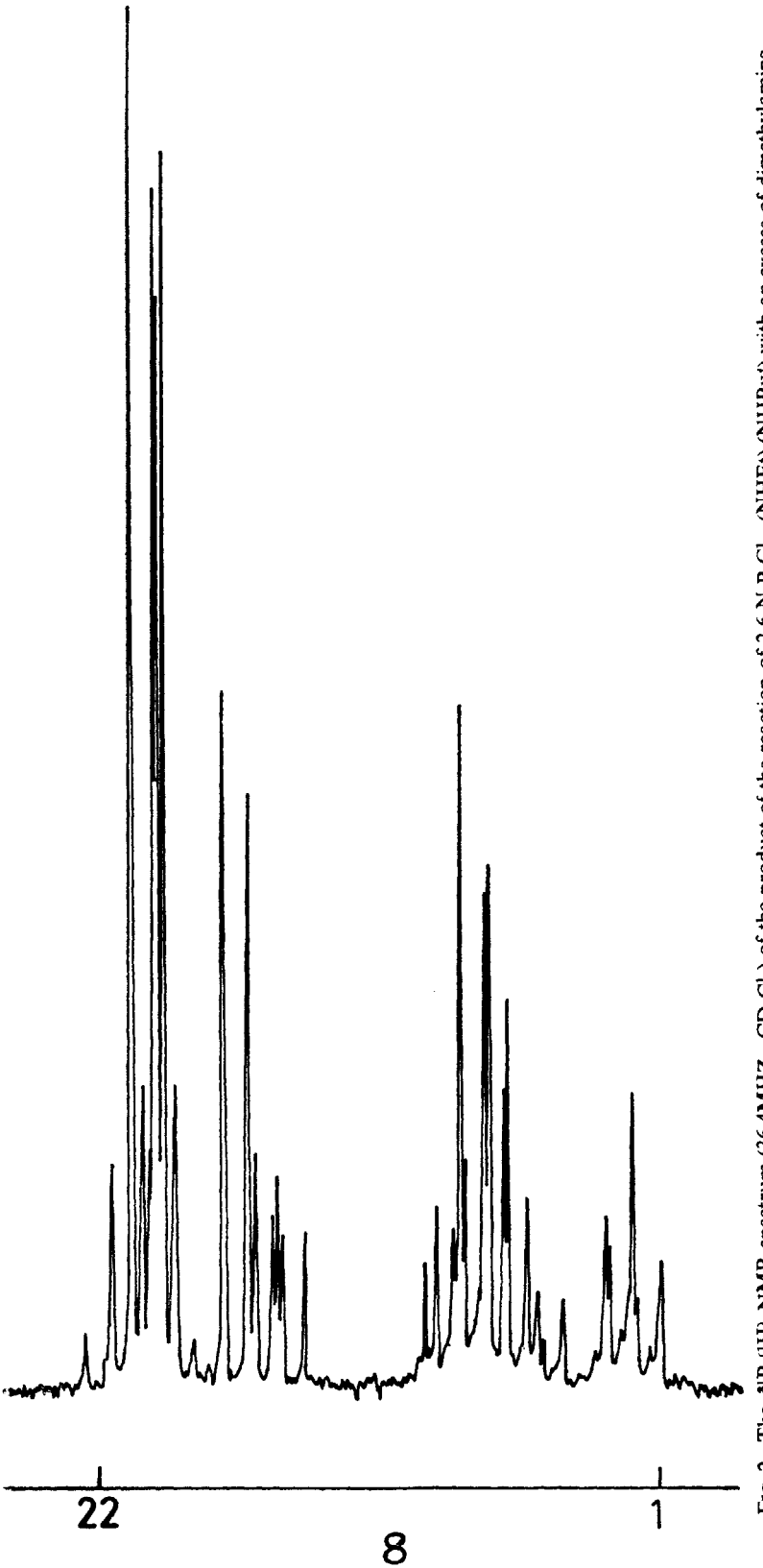


FIG 2 The ^{31}P $\{^1H\}$ NMR spectrum (36.4MHZ, CD_2Cl_2) of the product of the reaction of 2,6-$N_4P_3Cl_6$ (NHEt) (NHBu^t) with an excess of dimethylamine in chloroform after treatment with triethylamine. The low-field region (21-14δ) is due to the bicyclic derivative, $N_4P_4(NMe_2)_5$ (NHBu^t) (NEt) and the high-field region (9–1δ) is due to $N_4P_4(NMe_2)_6$ (NHBu^t) (NHEt). For parameters computed from the two halves of the spectrum, (see Ref. 21.)

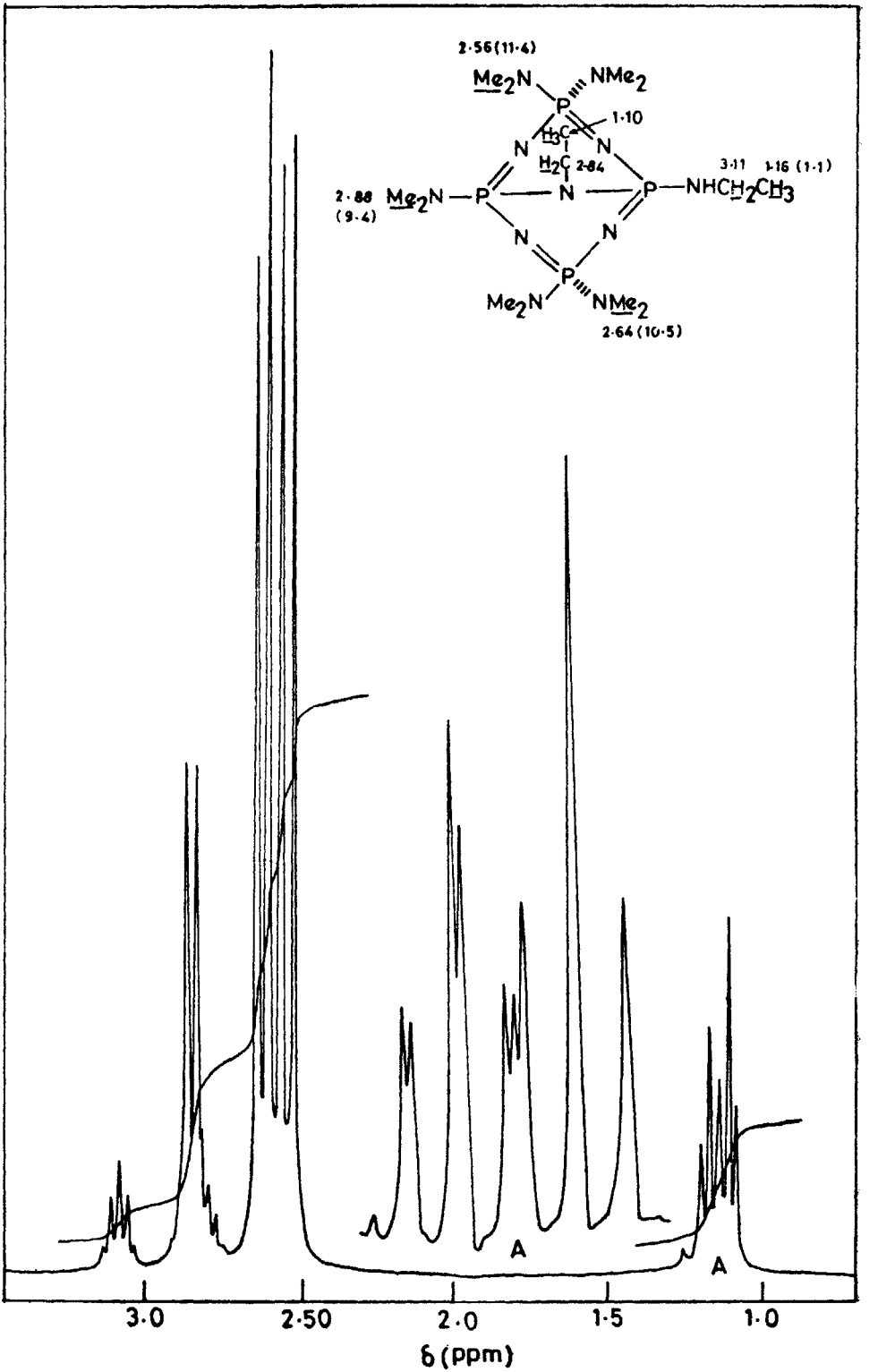


FIG 3 The 270 MHz ^{1}H NMR spectrum of VI ($R = R' =$ Et) in $CDCl_3$.

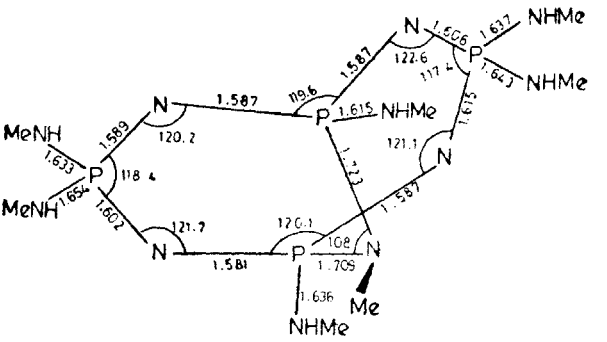
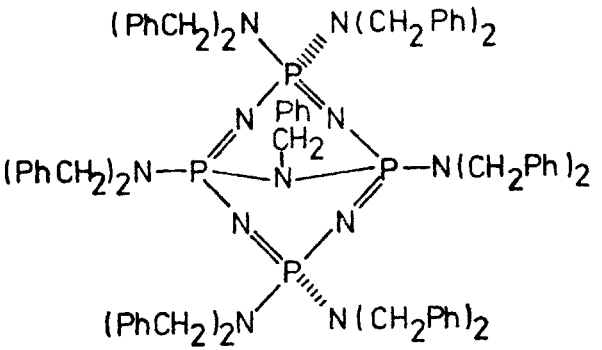


FIG 4 Structural data for the bicyclic phosphazene V(R = Me).

reveal several interesting features. The structural parameters for V(R = Me) is shown in Fig. 4. The fragments on either side of the bridge are approximately planar and the two planes are inclined at an angle of 122°. The molecular shape may be regarded as that of a basket. The peripheral P–N bonds retain their phosphazenic character. The P–N lengths at the bridgehead are longer (mean 1.716Å) and close to the length normally associated with a P–N single bond. The sum of the interbond angles at the bridgehead nitrogen atom is 336° which suggests that this nitrogen has a pronounced pyramidal character. Thus in bicyclic phosphazenes, the *trans*-annular bridging unit possesses essentially a phosphazene character.

A unique bicyclic compound, N_4P_4 [$N(CH_2PH)_2$]$_6$ (NCH_2Ph) (XIV) has been isolated in low yield from the reaction of $N_4P_4Cl_8$ (II) with an excess of dibenzylamine in boiling methyl cyanide.[28] This compound is characterised by high resolution mass spectrometry and IR and NMR spectroscopy. The formation of this unusual bicyclic compound must involve a dealkylation step prior to or concomitant with intramolecular nucleophilic attack.



XIV

The replacement of chlorine atoms from $N_4P_4Cl_8$ (II) by amino substituents, proceed mainly by the nongeminal pathway.[24,28,29-31] Substantial quantities of both 2,6 and 2,4-disubstituted products are formed with sluggishly reacting amino such as N-methylaniline,[30] dibenzylamine[28] *t*-butylamine[29b], neo-pentylamine,[22] benzylamine[24] or aniline[24]; more reactive amines (e.g. dimethylamine,[31] ethylamine[29(a)]) afford 2,6-substituted products almost exclusively. Only in two instances geminal substitution is observed. The reaction of $N_4P_4Cl_8$(II) with aqueous ammonia in diethyl ether in the presence of anhydrous sodium sulphate gives 2,2-$N_4P_4Cl_6(NH_2)_2$ (15 per cent)[32]; the reaction of II with aziridine in *n*-hexane affords 2,2-$N_4P_4Cl_6(NC_2H_4)_2$ (11 per cent).[33] Chloro(primary amino) cyclotetraphoshazenes containing both PCl(NHR) and $P(NHR)_2$ groups have not been identified. Attempts to prepare such derivatives lead to only resinous cross-linked materials.[29]

The $^{31}P\{^1H\}$ NMR spectra of 2,6- and 2,4-substituted *bits* (amino) cyclotetraphosphazenes are of the A_2B_2 and AA'BB' types respectively.[24] The spectra of the geminal derivatives, 2,2-$N_4P_4Cl_6R_2$($R = NH_2$, NC_2H_4) show asymmetric A_2BX patterns.[32,33]

The structures of the two isomeric *bis*-(N-methylanilino) derivatives, $N_4P_4Cl_6(NMePh)_2$ m.p 145 and 105 °C have been determined by single crystal X-ray diffraction. The highmelting isomer has a 2-*trans*-6 disposition of the amino substituents. The molecule is centrosymmetric and the P–N ring adopts the chair conformation.[34] The low-melting isomer has the 2-*trans*-4 structure; the P–N ring in this case assumes the boat conformation.[35]

Reaction of Chlorocyclophosphazenes with Difunctional Reagents

There are five possible pathways for the reaction of a halogenocyclophosphazene with an organic difunctional reagent as illustrated in Fig. 5 for $N_3P_3Cl_6$(I). All these pathways have been realised. We have demonstrated that the reactions of aliphatic diamines, $NH_2(CH_2)_nNH_2$(n = 2–4) with $N_3P_3Cl_6$(I) give initially the mono(spiro) derivatives, $N_3P_3Cl_4$ [$HN(CH_2)_n$ NH] (n = 2–4).[36,37] An X-ray diffraction study of $N_3P_3(NMe_2)_4$ ($NHCH_2CH_2NH$) confirmed its spirocyclic structure and hence that of its chloro precursor.[38] Further reaction of the mono (spiro) (ethane-1,2-diamino) tetrachloro derivative with 1,2-diamino ethane gives only a resinous material owing to a facile intermolecular condensation.[37] In contrast, both *bis*- and *tris*-spiro(propane-1,3-diamino) derivatives have been isolated from the reaction of $N_3P_3Cl_6$(I) with an excess of 1,3-diaminopropane.[36,39] Complete substiturion of the chlorine atoms of I has also been achieved with NN'-dimethylethylenediamine,[40] N-methyl ethanolamine[41] and numerous aliphatic diols.[42]

Labarre *et al.* have studied the reactions of I with $H_2N(CH_2)_n$ NH_2 (n = 3-5) in a mixed solvent medium. Only spirocyclic derivatives are formed when n = 3.[39] When n = 4, spirocyclic derivative[43] is the major product along with a ring-coupled derivative (XV, n = 4) as a minor product.[44] The intermolecular condensation product (XV) is formed exclusively when n = 5.[45] The

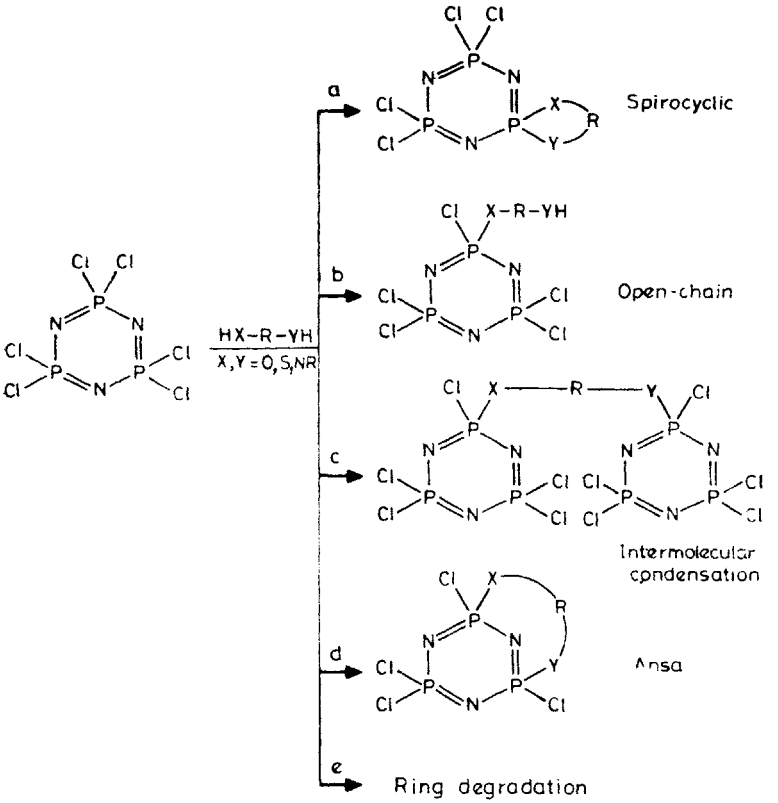
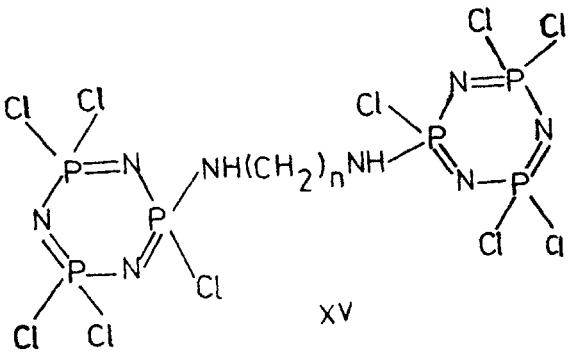


FIG 5 Possible pathways for the reaction of a halogenocyclophosphazene with organic difunctional reagents.

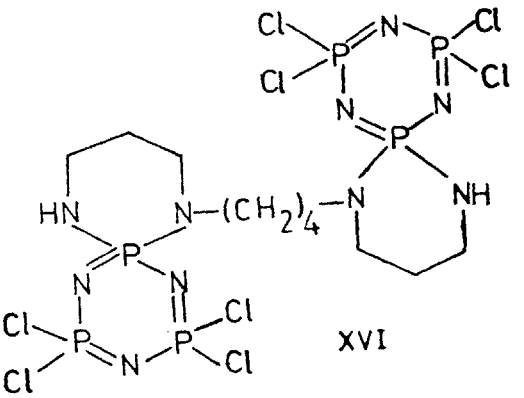
reaction of I with spermine is interesting in that it yields compound XVI which combines the features of spirocyclic and ring-coupled derivatives.[45,46] The importance of compouds of type XV and XVI lies in the fact that they are 'model' compounds for the synthesis of cyclolinear polymers.

The open chain pathway has been observed in a few systems[36] and a recent example is the propanolamino derivative XVII[46] reported by Harris and Williams who have also synthesised the first ansa compound (XVIII) starting from XVII.[46] Shaw *et al.* have isolated the spiro-ansa compound (XIX) which is isomeric to the *bis*-spiro derivative (XX).[47]

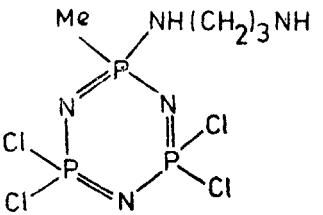
Two complementary methods have been explored for the synthesis of spirocyclic fluorocyclotriphosphazenes. The first method involves the reaction of $N_3P_3F_6$ with $H_2N(CH_2)_n NH_2$ ($n = 2, 3$) or HN(Me) $(CH_2)_2$ N(Me) H to obtain the monospiro derivatives.[48,49] The second method is more general and consists in the fluorination of mono(spiro) and di(spiro) chloro derivatives by using potassium fluoride in methyl cyanide.[48] The spirocyclic structures of the fluoro derivatives (and hence their chloro precursors) are readily established from the ^{31}P NMR data.



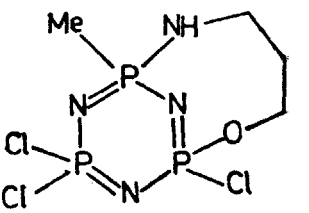
XV



XVI

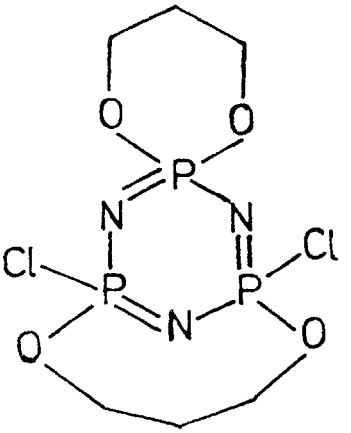


XVII

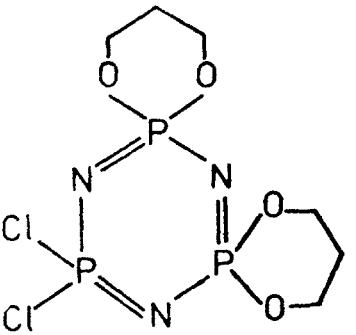


XVIII

Reactions of $N_3P_3Cl_6$(I) with *o*-phenylenediamine give spirocyclic derivatives whilst the *m*- and *p*-phenylenediamines give ring-coupled products.[1] Catechol,



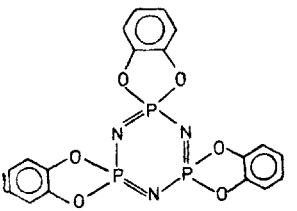
XIX



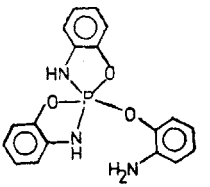
XX

3-methoxy catechol, 3-methoxy thiocatechol, 1,1′-dihydroxy 2,2′-binaphthyl and 2,2′-dihydroxy 1,1′-binaphthyl also give spirocyclic products.[1,50] Some of these spirocyclic phosphazenes (e.g. XXI) form inclusion clathrates with a variety of guest molecules[51] and this phenomenon can be used to advantage in polymerizing guest olefinic monomer molecules to obtain stereoregular polymers.[52,53]

Degradation of the P–N ring occurs in the reaction of $N_3P_3Cl_6$(I) with *o*-aminophenol ; the product is the phosphorane(XXII). The reaction of catechol yields an hexacoordinated phosphorus derivative, $[P(O_2C_6H_4)_3]^-(HNEt_3)^+$ in addition to spirocyclophosphazene.[1,3]



XXI



XXII

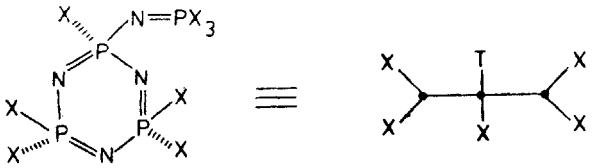
Structural aspects of spirocyclic derivatives have received considerable attention in recent years[38,41,43,54,55] and can be correlated with their ^{31}P chemical shifts.[41,55] The δ values of P_{spiro} incorporated in a 5-membered ring occur at a much lower field than those observed for P_{spiro} in compounds containing 6-or 7-membered rings. The 5-membered ring is subject to steric strain and as a consequence there is a decrease of π-electron release to the phosphorus atom from the exocyclic substituents.[41]

The reactions of $N_4P_4Cl_8$(π) with 1,2-diaminoethane or ethylene glycol yields a very unstable mono(spiro) cyclotetraphosphazene and a cross-linked resin. Treat-

ment of the former with dimethylamine gives the oxocyclotetraphosphazatriene, $N_4HP(O)(NMe_2)_7$. Reactions of $N_4P_4Cl_8$ with 1,3-diamino propane, 1,3-propane diol or N-methylethanolamine afford mono(spiro) cyclotetraphazenes which are conveniently characterised by ^1H and ^{31}P NMR spectra of their methoxy or dimethylamino derivatives, e.g. $N_4P_4(NMe_2)_6$ [$NH(CH_2)_3NH$] and $N_4P_4(OMe)_6$ [$O(CH_2)_3O$].[56] The NN'-dimethylethylenediamino derivatives, $N_4P_4X_6$ [N(Me) $(CH_2)_2$ N(Me)] (X = F,Cl) are also known.[49]

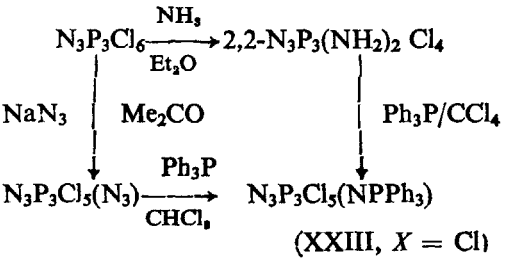
(Triphenylphosphazenyl) Cyclotriphosphazenes

Early reports of the reactions of pentachloro(triphenylphosphazenyl) cyclotriphosphazene(XXIII), X = Cl) with two equivalents of dimethylamine or piperidine in ether clearly showed that only the geminal product, $N_3P_3Cl_4R(NPPh_3)$ (R = NMe_2, NC_5H_{10}) was formed. This results was in contrast to the behaviour of these amines towards the mono(amino) derivative, $N_3P_3Cl_5R$, in which case the non-geminal derivative was formed almost exclusively[3]. The reactions of XXIII (X = Cl) with various amines have been investigated with a view to gaining a better insight into the substituent effect exerted by the -$NPPh_3$ group. The reactions of XXIII (X = F or Cl) with methoxide reveal significant differences in the halogen replacement pattern and serve to highlight the effect of leaving group on the displacement reactions at tetrahedral phosphorus centre.[57] Allcock *et al.* have made a similar comparative study of the reactions of $N_3P_3X_6$ (X = F, Cl) with metallocenyl anions.[58]



XXIII

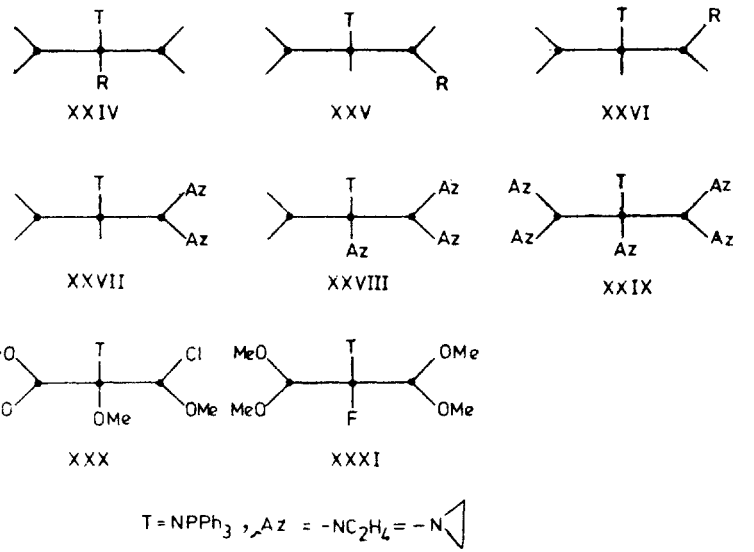
Two new methods have been developed for the synthesis of the chloro derivative XXIII (X = Cl) based on the Appel and Staudinger reactions :



(XXIII, X = Cl)

The fluoro derivative (XXIII, X = F) is conveniently prepared by the fluorination of the chloro precursor (XXIII, X = Cl) with potassium fluoride in methyl cyanide.[59]

The results obtained in the reactions of the chloro derivative (XXIII, $X = Cl$) with primary and secondary amines[60] may be summarised as follows. At the mono stage, secondary amines yield the geminal isomer of $N_3P_3(NPPh_3)$ $(R)Cl_4$ (XXIV, $R = NMe_2$, NEt_2, NC_5H_{10}) when diethyl ether or benzene is used as the solvent; reactions in methyl cyanide yield both geminal (XXIV) and nongeminal (XXV, XXVI) derivatives with the latter predominating. At the *bis* and subsequent stages of chlorine replacement a derivative of $N_3P_3(NPPh_3)$ R_nCl_{5-n} ($n \leqslant 2$, $R = NMe_2$, NEt_2, NC_5H_{10}) containing a $P(NPPh_3)Cl$ group is not formed. The



reaction of XXIII ($X = Cl$) with methylamine affords nongeminal isomers of $N_3P_3(NPPh_3)(NHMe)Cl_4$ exclusively in methyl cyanide and predominantly in ether. The results can be explained in terms of a change-over from a $S_N2(P)$ to a $S_N1(P)$ mechanism. Such a change-over is occasioned by the powerful electron releasing nature of the $-NPPh_3$ substituent as well as its steric bulk which would tend to retard an associative pathway. The formation of nongeminal products in a polar solvent such as methyl cyanide can be readily explained by postulating a one-step concerted $S_N2(P)$ mechanism (See Section G).

The reaction of XXIII($X = Cl$) with aziridine (HNC_2H_4) yields the partially and fully substituted derivatives $N_3P_3(NPPh_3)Cl_{5-n}(NC_2H_4)_n$ whereas the fluoro derivative (XXIII, X = F) is unreactive even under drastic experimental conditions.[61,62] At the *bis* stage of chlorine replacement, aziridine prefers to attack $P(NC_2H_4)Cl$ centre rather than PCl_2 or $P(NPPh_3)Cl$ centres to give XXVII. This result is in contrast to the behaviour of other secondary amines mentioned above. Presumably an $S_N2(P)$ mechanism operates at this stage because of the weaker basic character of aziridine compared to dimethylamine and also because the participation of the lone pair of electrons on the aziridino nitrogen atom in

π-bonding with the ring phosphorus atom is considerably less. The latter assumption is supported by the exocyclic P-N bond lengths (1.674 Å) and the appreciable pyramidal character of the aziridino nitrogen atom (sum of interbond angles 300°) in $N_3P_3(NC_2H_4)_6$.[63] At the *tris* stage of chlorine replacement, the geminal product (XXVIII) is formed exclusively as a result of a change-over from an associative to a dissociative S_N1 (P) mechanism.

The aziridino derivatives are of interest from the point of view of the reported anti-tumour activity of cyclophosphazenes and cyclothiaphosphazenes bearing aziridino groups.[11] The presence of an electron releasing group enhances the anti-tumour activity. A preliminary comparative study of the inhibition of the activity of the enzyme. Reverse Transcriptase (present in the virus *Avian myeloblastosis* which can cause leukaemia in chicks), by $N_3P_3(NC_2H_4)_6$ and $N_3P_3(NPPh_3)(NC_2H_4)_5$ (XXIX) shows that the latter is ~2.5 times more effective. The main disadvantage of the triphenyl phosphazenyl compound is its low solubility in DMSO or water.[62]

The successive replacement of chlorine atoms from $N_3P_3Cl_5(NPPh_3)$ by methoxide yields the geometrical isomers in unequal proportions (at the mono stage the *cis* isomer predominates) whereas the substitution of fluorine from $N_3P_3F_5(NPPh_3)$ under the same conditions gives the geometrical isomers in approximately equal proportions. The chlorine atom at the $P(NPPh_3)$ Cl centre is replaced readily and at the *tris* stage, the geminal derivative, $N_3P_3(NPPh_3)(OMe)_3Cl_2$ is formed almost exclusively. The fluorine at the $P(NPPh_3)$ F site is not replaced till the last stage. The two monohalogenotetra (methoxy) derivatives, $N_3P_3(OMe)_4(NPPh_3)$ $X(X = F, Cl)$ possess different structures; the chloro compound (XXX) contains a P(OMe) Cl group but the fluoro derivative (XXXI) contains a $PF(NPPh_3)$ and two $P(OMe)_2$ groups. The above differences can be explained in terms of a change-over from an associative to a dissociative mechanism for the methoxylation of $N_3P_3Cl_5(NPPh_3)$ and an associative mechanism persisting throughout for the fluoro system. The stereochemical course is difficult to explain. It is postulated that the attack of MeO^- on the fluoro compound (XXIII, $X = F$) occurs in the plane of the phosphazene ring.[57,64]

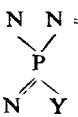
The $^{31}P\{^1H\}$ NMR spectra of triphenylphosphazenyl substituted cylophosphazene provide excellent examples of different types of a four-spin system and yield valuable structural information.[60,62,64,65] The conformations adopted by the $NPPh_3$ group with respect to the cyclophosphazene ring appears to be related to the sign and magnitude of four-bond P...P coupling constant.[66,67] The crystal structures of several (phosphazenyl) cyclotriphosphazenes have been determined mainly by Manohar *et al.*[67–71] and the data are summarised in Table I. Particularly noteworthy is the observation that in the structure of the pentaziridino derivative (Fig. 6), the N(4)–P(1)–N(9)–P(4) is 15° and the exocyclic P_4-N(9)-P(1) angle (145.3°) is the largest observed for (triphenylphosphazenyl) cyclotriphosphazenes. This unique conformation of the $NPPh_3$ group causes the protons of the geminal aziridino group to come into the shielding zone of one of the phenyl

TABLE I

Structural parameters for (phosphazenyl) cyclophosphazenes

Compound	Mean P(1)-N distance[a]	Mean P-N distance[b]	Exocyclic P-N distance[c]	Ring NPN angle[d]	Ring PNP angle[e]	Exocyclic PNP angle	Y-P-N-P' torsion angle[f]	Ref.
$N_3P_3Cl_5(NPPh_3)$	1.616	1.595	1.597 1.614	114.2 120.2	118.2 122.3	134.8	−83	68
$2,2\text{-}N_3P_3Cl_4Ph(NPPh_3)$	1.625	1.584	1.576 1.585	111.7 120.2	118.4 123.1	131.6	−178	*g*
$2,2\text{-}N_3P_3Cl_4(NEt_2)(NPPh_3)$	1.633	1.583	1.563 1.585	109.9 120.6	117.5 125.1	137.6	154	67
$2\text{-trans-}4\text{-}N_3P_3Cl_4(NEt_2)(NPPh_3)$	1.61	1.560	1.56 1.57	114.5 119.1	118.6 121.8	140.6	65	71
$N_3P_3(NC_2H_3)_5(NPPh_3)$	1.609	1.584	1.557 1.589	114.0 117.1	122.7 123.5	145.3	15	62
$2,2\text{-}N_3P_3Cl_4(NPPh_3)_2$	1.642	1.562	1.558 1.601	109.2 120.8	117.5 119.0	134.3	6.7 −176.7	70
$N_4P_4Cl_7(NPPh_3)$	1.590	1.555	1.588 1.563	115.4 122.4	133.5	133.0	−58	69
$N_3P_3Cl_5[NPCl(\eta\text{-}C_5H_4Fe\eta\text{-}C_5H_5)_2]$	1.606	1.566	1.566 1.537	114.2 120.6	117.7 122.5	142.7	—	*h*

a P(1) is the phosphorus carrying the NPX_3 group
b Mean of other ring P-N distances
c The first value is for $X_3P = N$
d The first value is for P(1)
e The first value is for nitrogen opposite P(1)
f



g M Biddlestone R A Shaw G J Bullen and P E Dann *J chem Soc chem Commun* (1974), 56.
h H R Allcock K-D Levin G H Riding and R R Whittle *Organometallics* **3**, (1984), 663.

rings and thereby renders these protons the most shielded ones. Generally, for the fully substituted triphenylphosphazenyl derivatives, $N_3P_3(NPPh_3)$ $R_5(R = OMe, OCH_2CF_3, NMe)$, the shielding sequence of the three different types of protons is *cis*> *gem* > *trans*.[62]

ALKOXY/ARYLOXY CYCLOPHOSPHAZENES

(Alkoxy) and (aryloxy) cyclophosphazenes have acquired great practical value owing to their hydrolytic and thermal stability. Various aspects of their chemistry and applications have been surveyed.[1,3,10] The use of an aryloxy substituent as a blocking group to reduce the functionality of cyclophosphazene precursors may offer significant advantages in the synthesis of polymers. We have carried out a

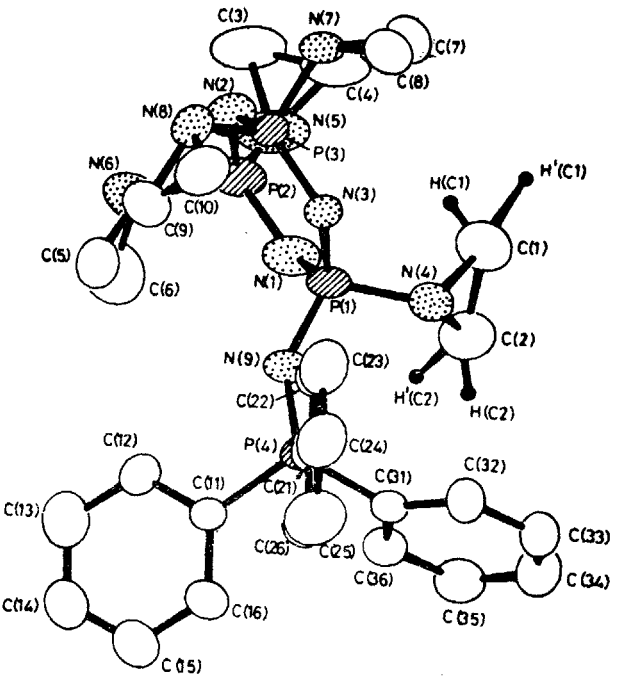


FIG 6 The structure of $N_3P_3(NC_2H_4)_5(NPPh_3)$ (XXIX).

systematic study of the reactions of $N_3P_3Cl_6$ with sodium phenoxide and *p*-cresoxide[72] and the reaction of $N_3P_3F_6$ with sodium phenoxide.[73] The halogen replacement is predominantly nongeminal but the stereochemical course followed in the chloro and fluoro systems are different (F. 7). A "through space" interaction involving the oxygen-2p and phosphorus-3d orbitals is invoked to explain the slightly greater yield of the *cis* isomer of $N_3P_3Cl_4(OAr)_2$ compared to that of its *trans* counterpart.[72] The reaction of $N_3P_3F_6$ can be conveniently monitored by GLC.[73]

The reaction of $N_4P_4Cl_8$(II) with phenoxide (or $PhOH + Et_3N$)[74] or trifluoroethoxide[75] are much more complex than the analogous reactions of $N_3P_3Cl_6$(I). More than twenty chloro(trifluoroethoxy) cyclotetraphosphazenes have been identified by GC-MS analysis of the reaction mixtures obtained by varying the stichiometry of the reactants. The chlorine replacement pattern with phenoxide is largely nongeminal; at the *bis* stage the 2,4-substituted derivative is favoured over the 2,6-substituted product. At the hexakis stage, there is a distinct preference for the 2-*trans*-6 isomer. With trifluoroethoxide, substantial amounts of products containing $P(OCH_2CF_3)_2$ group(s) are formed at the *tris* and subsequent stages of chlorine replacement. The behaviour of the trifluoroethoxide is intermediate between that of phenoxide[74] and fluoride ions.[3] An important observation in this study is the steady increase in volatility and the drastic decrease in GLC retention times with increasing degree of substitution by trifluoroethoxy groups. Thus GLC

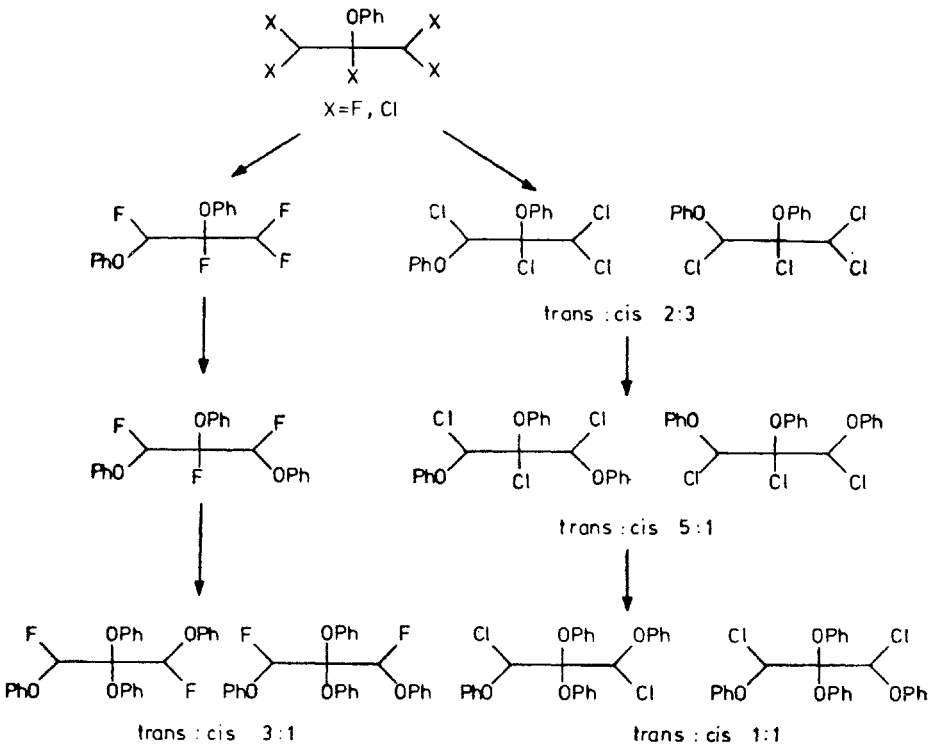


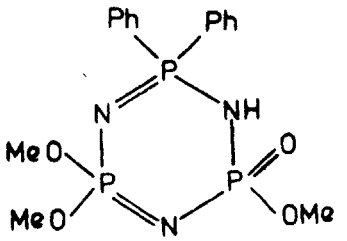
FIG 7 The halogen replacement pattern in the reactions of $N_3P_3X_6$(X = F, Cl) with phenoxide.

technique may prove useful for analysis of chlorocyclophosphazene mixtures after converting them into their trifluoroethoxy derivatives.

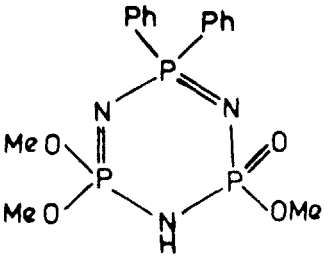
"HYDROXY" CYCLOPHOSPHAZENES-THEIR PROTOTROPIC BEHAVIOUR AND REACTIONS

Several "hydroxy" cyclophosphazenes, $N_3P_3R_5(OH)$ (R = OMe, OPh, Ph), $N_3P_3Ph_2(OR)_3$ (OH) (R = Me, Et, Pr^n and $N_3P_3(NHBu^t)_2(OR)_3$ (OH) (R = Me, Et) have been prepared and their tautomeric behaviour elucidated by dynamic ^{31}P NMR spectroscopy.[76] All these derivatives exist as oxophosphazadiene tautomers in which the hydrogen atom is attached to a ring nitrogen atom adjacent to the phosphoryl group. The crystal structure of the diphenyl derivaitve, $N_3P_3PH_2(OMe)_3$ (OH) shows that the molecule exists as a hydrogenbonded dimer of the oxophosphazadiene tautomeric form (XXXII) in which the proton is attached to the nitrogen atom adjacent to PPh_2 group.[77] However, in solution, there is a rapid exchange between the two tautomers(XXXII, XXXIII) at ambient temperature with the former in greater abundance.[76]

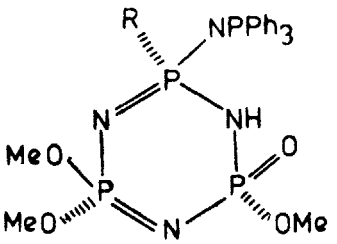
Recently, the mono "hydroxy" derivatives, $N_3P_3(NPPh_3)$ (R) $(OMe)_3$ (OH) (R = OMe or NMe_2) have been isolated. High field ^1H and ^{31}P NMR data reveal that they exist as a pair of *cis* and *trans* (with respect to phosphoryl and



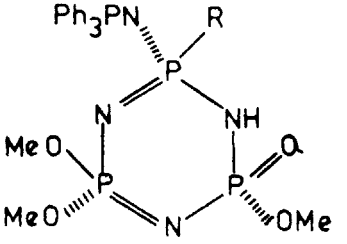
XXXII



XXXIII



XXXIV

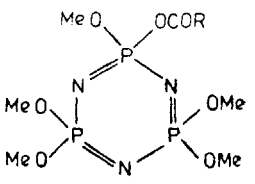


XXXV

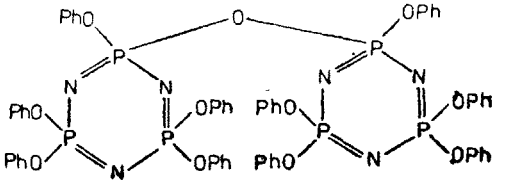
$NPPh_3$ group) oxophosphazadienes (XXXIV, XXXV). Protonation occurs at the nitrogen adjacent to $P(NPPh_3)$ (*R*) site and there is no exchange of the hydrogen among the skeletal nitrogen atoms.[78]

"Hydroxy" cyclophosphazenes can be readily prepared by the reactions of (alkoxy) cyclophosphazenes with iodotrimethyl silane.[79]

Although "hydroxy" phosphazenes exist as their oxophosphazadiene tautomers, they react with acid chlorides to yield phosphazene carboxylate derivatives (e.g. XXXVI).[80] They also react with chlorocyclophosphazenes in the presence of a base to yield P-O-P bridged compounds (XXXVII).[81]



XXXVI



XXXVII

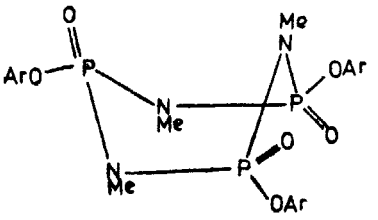
Thermal Rearrangement of (Alkoxy) Cyclophosphazenes

The (methoxy) cyclophosphazenes, $[NP(OMe)_2]_n$ ($n = 3$–6) rearrange on heating to give the oxocyclophosphazenes, $[N(Me)\ P(O)\ (OMe)]_n$. Isomeric products are formed when $n = 4$–6. The ethoxy and *n*-propoxy derivatives do not undergo the above rearrangement thermally; resinous materials are obtained

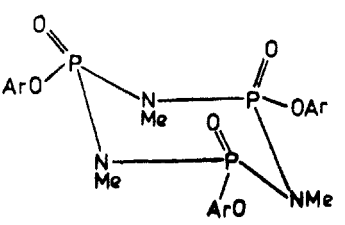
which are presumably P-O-P cross-linked polymers. The geminal derivatives, $N_3P_3R_2(OMe)_4$ (R = Ph, NHBu^t) on heating at 150–200 °C yield both fully and partially rearranged products *viz.* di (oxo) phosphaza-1-enes and oxophosphazadienes.[82]

In order to further elucidate the effect of other substituents on the above rearrangement reaction and also to unravel the mechanistic aspects, the thermal rearrangement of (alkoxy) (*p*-cresoxy) cyclotriphosphazenes, $N_3P_3(OMe)_{6-n}(OC_6H_4Me\text{-}p)_n$ (n = 1–5) and $N_3P_3(OR)_3$ $(OC_6H_4Me\text{-}p)_3$ (R = Et, CH_2Ph) have been investigated recently.[79] A single rearranged product is obtained in all cases except in the case of mono(*p*-cresoxy) penta(methoxy) darivative, which yields two isomers. An increase in the number of aryloxy groups causes an increase in the rearrangement temperature (160–225 °C). The reactions are conveniently monitored high-field ^1H and ^{13}C NMR spectroscopy.[79,82]

The rearrangement of *cis* or *trans*-$N_3P_3(OC_6H_4Me\text{-}p_3$ $(OMe)_3$ proceeds stereospecifically and for the first time a pair of isomeric oxocyclotriphosphosphaze nes has been isolated. An X-ray crystallographic investigation of the *trans* isomer shows that the P-N ring exists in a twist-boat conformation (XXXVIII).[83] A chair conformation is proposed for the *cis* isomer (XXXIX) on the basis of NMR data.[79]



XXXVIII



XXXIX

Mechanism of Nucleophilic Substitution Reactions of Halogenocyclophazenes : Kinetic Studies

Although there have been a large number of synthetic studies of the nucleophilic substitution reactions of halogenocyclophosphazenes, kinetic studies to elucidate the mechanisms of these reactions have been carried out only in recent years. These studies relate to aminolysis and alkoxylation reactions of halogenocyclophosphazenes, the hydrolysis of chloro, alkoxy, aryloxy or amino cyclophosphazenes and metathetical exchange reactions.[1,3,84-90] The results obtained in our laboratory on carefully chosen systems have enabled us to gain a better insight into the mechanisms of these reactions.

The rates of stepwise replacement of chlorine atoms from $N_3P_3Cl_6$ by NMe_2 group in methyl cyanide have been determined. The activation parameters (Table II) indicate that whereas a $S_N2(P)$ mechanism involving a five-coordinated phosphorus intermediate operates for the first chlorine substitution (Fig. 8a), the

TABLE II

Kinetic data for the reactions of halogenocyclophosphazenes with various amines[a]

Cyclophosphazene	Amine	Solvent	Second order rate constant[b] $k_2/dm^3\ mol^{-1}\ Sec^{-1}$	ΔH kJ mol^{-1}	ΔS J $ml^{-1}\ K^{-1}$	Ref
$N_3P_3Cl_6$	$HNMe_2$	MeCN	105.7	20.7	—128.0	88
$N_3P_3Cl_5(NMe_2)$	$HNMe_2$	MeCN	32.4	10.6	—189.7	88
2-*trans*-4-$N_3P_3Cl_4(NMe_2)_2$	$HNMe_2$	MeCN	2.21	14.0	—196.4	88
$N_3P_3F_6$	$HNMe_2$	MeCN	8.27	53.1	—128.7	88
$N_3P_3Cl_6$	Bu^tNH_2	MeCN	9.7×10^{-3}	20.3	—205.7	87
$N_3P_3Cl_6$	Bu^tNH_2	thf	1.9×10^{-3}	47.6	—125.9	87
$N_4P_4Cl_8$	Bu^tNH_2	MeCN	2.28	8.2	—201.6	87
$N_3P_3Cl_6$	$PhNH_2$	MeCN	2.09×10^{-3}	29.1	—203.9	91
$N_3P_3Cl_6$	$ArNH_2$[d]	MeCN	2.67×10^{-2} [c]	25.2	—189.5	91
$N_3P_3Cl_6$	$ArNH_2$[d]	thf	1.92×10^{-3}	21.9	—261.7	91
$N_3P_3Cl_5(NHAr)$[d]	$ArNH_2$[d]	MeCN	5.05×10^{-4}	33.6	—196.3	91
$N_3P_3Cl_5(NHAr)$[d]	$ArNH_2$[d]	thf	1.19×10^{-4} [e]	29.1	—278.2	91
gem-$N_3P_3Ph_2Cl_4$	H_2NMe	MeCN	0.50	28.1	—154.4	22
gem-$N_3P_3Ph_2Cl_4$	H_2NMe	thf	0.154	19.9	—191.9	22
gem-$N_3P_3Ph_2Cl_4$	$HNMe_2$	MeCN	1.24	10.2	—207.6	22
gem-$N_3P_3Ph_2Cl_4$	$HNMe_2$	thf	8.28×10^{-2}	18.7	—201.4	22

a Error involved in the parameters 5 per cent
b at 20 °C unless specified otherwise
c at 25 °C
d Ar = $C_6H_4(OMe)$-*p*
e at 30 °C

data for the second and third chlorine substituion are better accommodated by a one-step concerted mechanism (Fig. 8b). A sharp change-over from an $S_N2(P)$ to a $S_N1(P)$ mechanism (Fig. 8c) occurs at the tetrakis stage of chlorine replacement. With increasing degree of substitution, the attainment of a transition state with a five-coordinated phosphorus becomes difficult; at the same time the mesomeric electron release by the three amino substituents into the phosphazene ring facilitates the hetrolysis of the P-Cl bond. The $S_N1(P)$ mechanism has also been established for the replacement of the lone chlorine atom from $N_3P_3(OPh)_5$ Cl by NMe_2 or NHMe group.[88]

The reactions of $N_3P_3Cl_6$(I) and $N_4P_4Cl_8$(II) with *t*-butylamine in methyl cyanide follow a bimolecular mechanism *via* penta-coordinated phosphorus intermediate.[87] The reactivity of the eight-membered ring is ~ 200 times greater than the six-membered ring; this enhanced reactivity stems from the greater skeletal flexibility of the former.

Kinetic studies of the reactions of the geminal diphenyl derivative, $N_3P_3Ph_2Cl_4$ with dimethylamine and primary alkyl amines have been carried out in both methyl cyanide and tetrahydrofuran (thf).[22] Whilst methylamine reacts faster than dimethylamine in thf, the reverse trend is observed in methyl cyanide. The rate

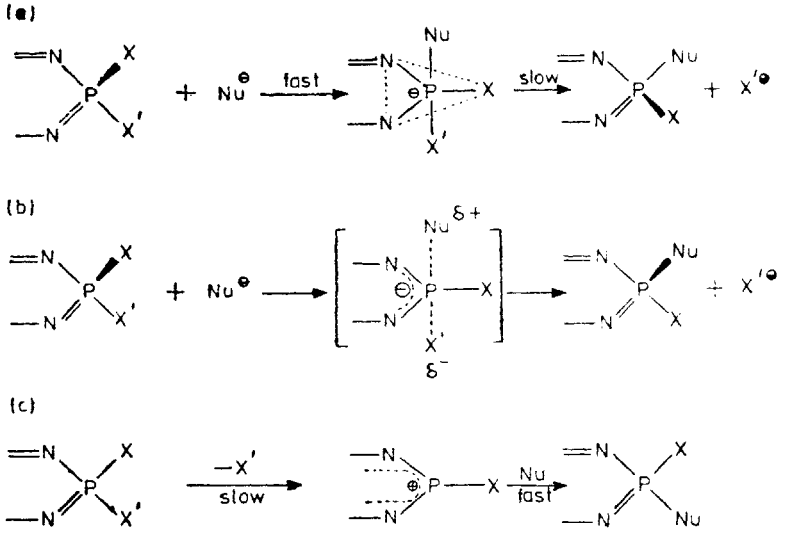


FIG 8 The mechanism of nucleophilic displacement at a tetrahedral phosphorus (*a*) $S_N2(P)$ mechanism involving a penta-coordinated intermediate, (*b*) one-step concentrated $S_N2(P)$ mechanism (*c*) $S_N1(P)$ mechanism.

data as well as the activation parameters suggest that in a polar solvent such as methyl cyanide the concerted mechanism prevails; in thf, which is less polar, the reaction proceeds essentially via neutral penta-coordinated intermediate.

The rates of the reactions of $N_3P_3Cl_6(I)$ with aromatic primary amines (aniline, *p*-toluidine and *p*-anisidine) have been determined. The data indicate that the first and second stages of chlorine replacement proceed by a bimolecular mechanism in both thf and methyl cyanide. In both the solvents, the nongeminal *bis*(amino) derivative (1 : 2 mixture of *cis* and *trans* isomers) is formed almost exclusively. However, in the presence of an excess of tri-*n*-butylamine, the replacement of the second chlorine atom occurs by an E_1CB mechanism which involes the intermediacy of a three-coordinated P^v species (XXXX) (Fig. 9). The sole product is the geminal *bis*(amino) derivative (XXXXI). The reaction obeys a pseudo first order rate law with respect to $N_3P_3Cl_5(NHAr)$; the pseudo first-order rate constant (k') varies linearly with the initial concentration of tri-*n*-butylamine. The intermediacy of the phosphoramidate type 3-coordinated P^v species (XXXX) has been conclusively established by trapping it with methanol (XXXXIII) and by the isolation of the unusual product, *gem*-$[N_3P_3Cl_4(NHC_6H_4R\text{-}p)\ O]^-\ (NHEt_3)^+$ (XXXXII)[91] as shown in Fig. 9. The $^{31}P\ \{^1H\}$ NMR spectrum of XXXXII (R = Me) is shown in Fig. 10.

All the possible pathways for nucleophilic displacement at a tetrahedral phosphorus centre have now been realised in cyclophosphazene systems. The mechanistic studies enable us to understand the combined role of the substituent present on the phosphazene ring, the reacting nucleophile, the leaving group and

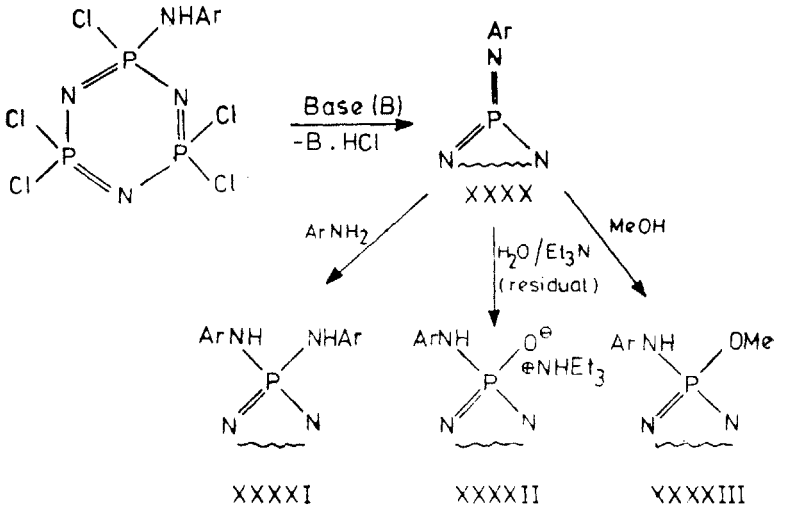


FIG 9 The generation and trapping of a phosphoramidate species, $N_3P_3Cl_4NR$(XXXX).

the reaction medium on the nature of the products formed in the substitution reactions of cyclophosphazenes.

PHOSPHAZENE POLYMERS

Poly (organophosphazenes) possess a number of unusual properties which make them superior to other hetero atom polymer systems. Basic research in this field has developed rapidly in recent years and phosphazene based polymers are now poised on the threshold of being considered for a variety of technological applications.[12–14]

We have investigated several approaches for the synthesis of phosphazene polymers. These include the conventional methods of ring-opening thermal polymerization of $N_3P_3Cl_6$[14] (using several new initiators such as salt hydrates and substituted cyclophosphazenes) and condensation polymerization involving the reactions of chlorocyclo-phosphazenes with aromatic diamines and diols.[19] Two new methods have been developed based on the strategy of "side-group modification" reactions. One method exploits the facile cleavage of PO-alkyl bonds by iodosilanes which leads to the incorporation of phosphazene rings into siloxane chains (Fig 11). However, the resulting polymers are prone to hydrolytic decomposition.[79] The second approach utilizes the reactions of (aryloxy) phosphazenes with polyhaloalkanes under Friedel Crafts conditions to obtain cross-linked phosphazene polymers that posses high thermal stability. This method (Fig. 12) holds considerable promise for synthesising phosphazene polymers with varied properties.[92]

CONCLUDING REMARKS

It has been generally believed that the halogen replacement pattern in the substitution reactions of cyclo-phosphazenes is dependent only on the nature of the

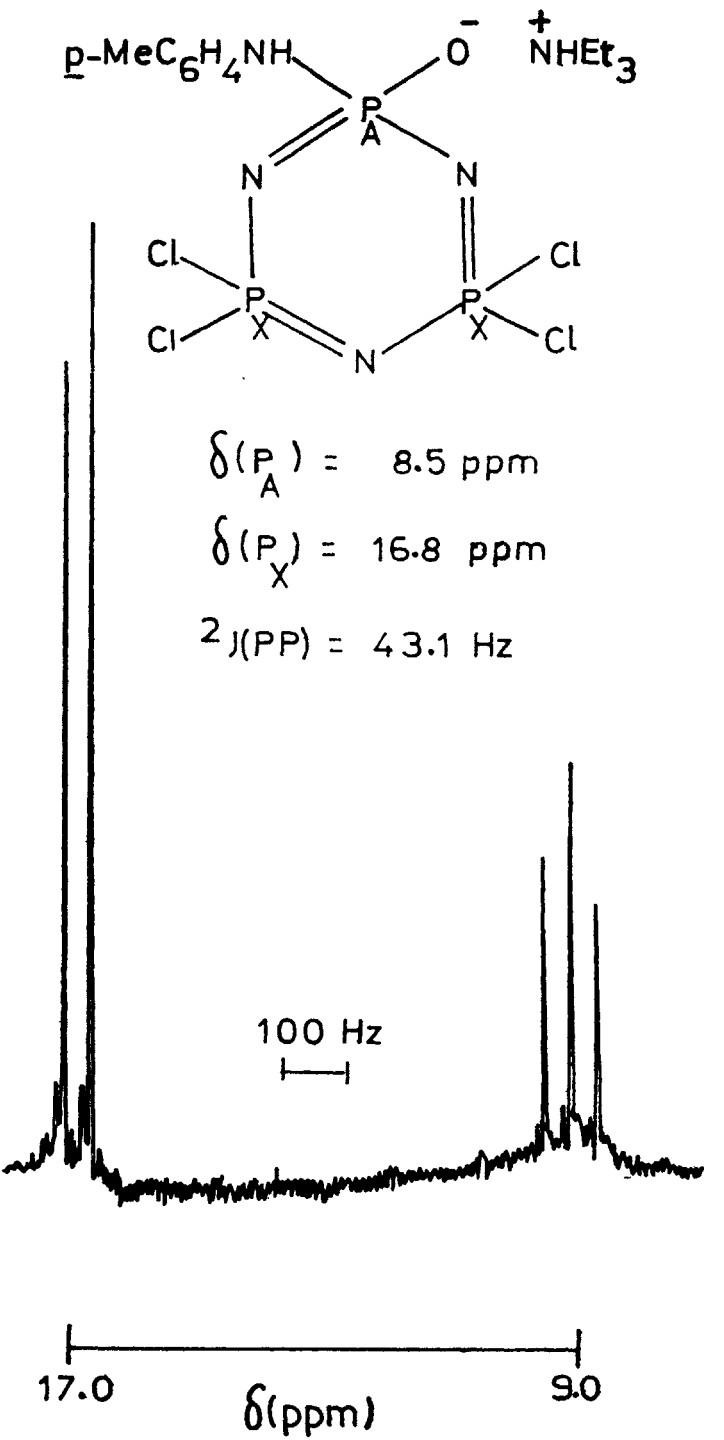


FIG 10 The ^{31}P {^{1}H} NMR spectrum (32 MHz, $CDCl_3$) of the triethylammonium salt (XXXXII, R = Me).

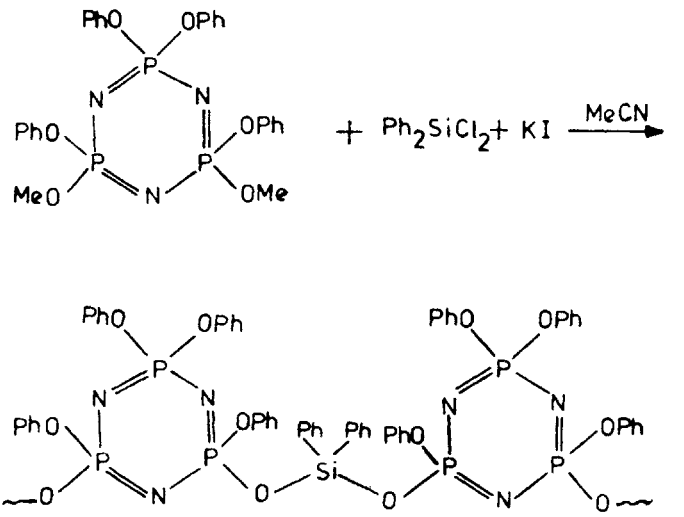


FIG 11 Reaction of alkoxy phosphazenes with iodosilanes to yield polymers incorporating phosphazene rings into siloxane chains.

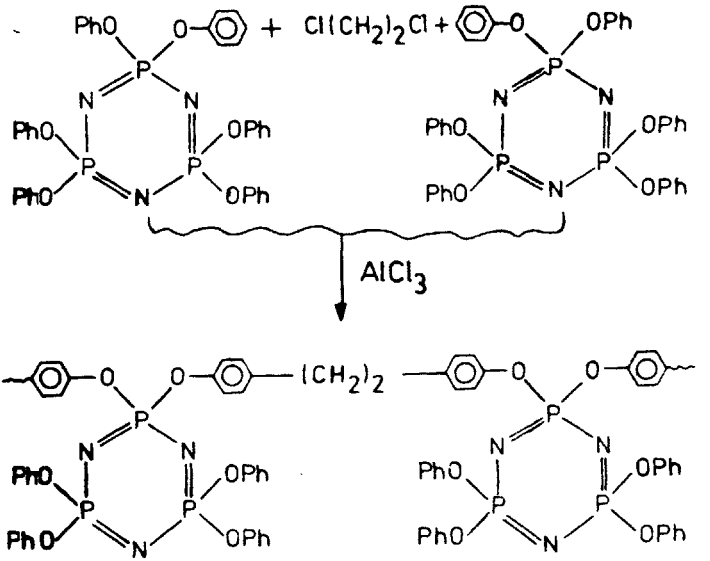


FIG 12 Friedel Crafts condensation of aryloxy groups in $N_3P_3(OPh)_6$ with $Cl(CH_2)_2Cl$ (For simplicity only one aryloxy group is included in the cross-linking process; cross-linking can also occur through the *ortho* positions).

attacking nucleophile and not on the substituent already present on the phosphazenes ring.[3] Our studies reviewed in this paper have exposed the limited validity of the above simplistic hypothesis. The type of mechanism and hence the nature of products formed are determined by the combined effect of the substituent(s) attached

to the P–N ring, the incoming nucleophile, the leaving group and the reaction medium. The results have important ramifications in the context of a great deal of current interest evinced in the stereochemistry of nucleophilic displacement at a tetrahedral phosphorus and its analogy to silicon systems.[93]

Several subtle aspects of the mechanism of formation of *trans*-annular bridged bicyclic phosphazenes derived from chloro (primary amino) cyclotetraphosphazenes have been unravelled and a directed synthetic strategy has been developed for bicyclic phosphazenes containing different amino substituents.

Cyclophosphazenes, with varying ring size and shape, offer some of the best examples of multi-spin systems. Their NMR spectra, besides being of interest to NMR specialists, would be very useful for instructional purposes. This aspect has not received adequate attention so far. A comprehensive understanding of the phosphorus–31 chemical shifts and P...P coupling constants is also lacking although some general trends have been noted.[94]

The range and versatility of the reactions undergone by cyclophazenes ensures that a considerable amount of new and fascinating chemistry will be developed, particularly in the areas of organometallic chemistry of cyclophosphazenes[6,7,58,95] and phosphazene polymer chemistry.[12-14]

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