Synthesis of Some Amino-, Ethyleneglycolato- & N,N'-Dimethylethylenediamino-cyclophosphazenes

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Chloramination of phosphorus trichloride, 2-chloro-1,3,2-dioxaphospholane and 1,3-dimethyl-2-chloro-1,3,2-diazaphospholane in the presence of ammonia has been investigated as a route for the direct synthesis of amino-cyclophosphazenes and ethyleneglycolato- and N,N'-dimethylethylenediamino-spirocyclophosphazenes. It has been found that the steric requirements and electronic nature of the side substituents, attached to phosphorus atom, seriously interfere in the direct conversion of chlorophosphine substrates to the phosphazene skeleton by chloramine-ammonia mixture. Whereas oxidation of phosphorus trichloride by chloramine-ammonia mixture yields the octa-aminocyclotetraphosphazene, [NP(NH$_2$)$_3$]$_4$, the 2-chloro-1,3,2-dioxaphospholane is exclusively converted into the spirotris-1,1,3,3,5,5-ethyleneglycolatocyclotriphosphazene(I). However, 1,3-dimethyl-2-chloro-1,3,2-diazaphospholane yields only 2,2-diamino-1,3-dimethyl-1,3,2-diazaphospholanium chloride (II) which unlike dialkyl- or diphenyl-diaminophosphonium chlorides fails to give cyclic or linear phosphazenes under pyrolytic condensation.

DIRECT oxidation of diphenylchlorophosphine (C$_6$H$_5$)$_2$PCl, by NH$_2$Cl-NH$_3$ mixture to the hexaphenyldicyclopentaphosphazene, [(C$_6$H$_5$)$_3$PN]$_3$, is a cornerstone in the phosphazene synthesis$^1$. The route is applicable to dialkylchlorophosphines which yield dialkyldiaminophosphonium chlorides, [R$_2$P(NH$_2$)$_2$]Cl$^-$ (where R=CH$_3$, C$_2$H$_5$, and n-C$_4$H$_9$) and/or their self-condensation to nitrilo-bis(dialkylphosphonium chloride intermediates, [(NH$_2$)$_2$R]$_3$P=N-PR$_2$(NH$_2$)$_2$Cl$^-$, which undergo pyrolytic condensations to lead to the formation of cyclic and linear phosphazene homologs$^2$-$^3$. Thus, the synthesis of poly(di-methylphosphazene), [(CH$_3$)$_3$PN]$_n$, with n=170 by Sister and coworkers$^4$ employing pyrolytic condensation of dimethylaminophosphonium chloride represents a remarkable route for the industrially useful phosphazene macromolecules. The proven fertilizer potential of the hexa-aminocyclotetraphosphazene, [NP(NH$_2$)$_3$]$_4$, and possibility of variation of the agronomical properties in the higher cyclic and linear homologs$^5$ led to the direct synthesis of these aminophosphazenes by the chloramination route from PCl$_5$ and of spirocyclophosphazenes from 2-chloro-1, 3,2-dioxaphospholane and 1, 3-dimethyl-2-chloro-1,3,2-diazaphospholane$^6$.

In this paper, the synthesis of octa-aminocyclotetraphosphazenes, [NP(NH$_2$)$_3$]$_8$, and spirotris-1, 3: 5, 5-ethyleneglycolatocyclotriphosphazene(I) by the action of NH$_2$Cl-NH$_3$ on PCl$_5$ and 2-chloro-1,3,2-dioxaphospholane, respectively, is reported. Implications of the electronic structure and steric requirements of the side substituents, attached to phosphorus, have also been examined in relation to the direct conversion of chlorophosphine substrates by NH$_2$Cl-NH$_3$ mixture to the cyclic and linear phosphazene homologs.

The present study demonstrates that chloramination route is extendable to the direct synthesis of aminocyclophosphazenes and spirocyclophosphazenes. A reaction sequence in which the corresponding phosphonium and nitrilo-bisphosphonium chloride intermediates are formed by chloramination following the ammonolysis of chlorophosphine substrate and undergo condensation to the phosphazene framework can be assumed for the present synthesis in accordance with the studies of the R$_2$PCI-NH$_2$Cl-NH$_3$ (where R=CH$_3$, C$_2$H$_5$, n-C$_4$H$_9$, and C$_6$H$_5$) systems$^1$-$^2$. This scheme for the formation of I is represented by Eqs (1-5) (Chart I).

Analogous reaction sequence for the formation of octa-aminocyclotetraphosphazene following the ammonolysis of PCl$_5$ to P(NH$_2$)$_6$ can be assumed. The formation of 2,2-diamino-1,3-dimethyl-1,3,2-diazaphospholanium chloride (II) from the corresponding phospholane proceeds analogous to Eqs (1) and (2) (Chart I). Unlike other chlorophosphine substrates, there is no evidence for the direct formation of cyclic and linear phosphazenes or nitrilo-bisphosphonium chloride intermediate in the chloramination of 1,3-dimethyl-2-chloro-1,3,2-diazaphospholane in the presence of ammonia. Under the experimental conditions, II does not yield to pyrolytic conversion to the phosphazenes. In this
and earlier studies of Sisler and co-workers\textsuperscript{1-3}, a marked difference is noted in the reactivities of chlorophosphines with chloramine-ammonia mixtures with respect to direct conversion of the phosphonium chloride intermediates to the phosphazenes or under pyrolytic conditions. Two most notable cases are of diphenychlorophosphine and 2-chloro-1,3,2-dioxaphospholane in which conversion to the trimeric P\textsubscript{3}N\textsubscript{3} ring occurs under mild conditions and is attributed to the electron withdrawal effects of the phenyl and ethyleneglycolato groups attached to the phosphorus atom which would have a stabilizing influence on the phosphazene ring by contributing to the in-plane pi-bonding. In the reactions of dialkylichlorophosphines and 2-chloro-1,3,2-dioxaphospholane, stable phosphonium chlorides are isolated\textsuperscript{3}. No such intermediates have been isolated from the chloramine-ammonia reactions with diphenychlorophosphine and 2-chloro-1,3,2-dioxaphospholane. Whereas condensation of phosphonium chlorides of the latter chlorophosphines occurs readily even under mild conditions presumably due to gain in pi-stability of the phosphazene skeleton, the dialkylaminophosphonium chlorides require forcing conditions for conversion to cyclic and linear phosphazenes. Thus, electron donation by the alkyl or amino groups appears to contribute to the pyrolytic stabilities of these phosphonium chlorides with respect to their conversion to phosphazenes. Although dialkylaminophosphonium chlorides yield to pyrolytic decomposition to the cyclic trimer and tetramers\textsuperscript{4} and poly (dimethylphosphazene) macromolecule with 170 repeating PN units,\textsuperscript{5} the 2,2-diamino-1,3-dimethyl-1,3,2-diazaphospholanium chloride (II) does not decompose appreciably even after 48 hours of heating at 161-163\textdegree C in high vacuum. Traces of ammonium chloride, cosublimed with phospholanium chloride, does indicate that some condensation occurred but no evidence for any phosphazene formation could be found. Whether it is the steric crowding around phosphorus in phospholanium chloride or the steric hindrance due to disposition of methyl group in the phosphazene framework which prevents self-condensation of phospholanium chloride to cyclic or linear phosphazenes is not resolved. From the molecular weight data of Utvary\textsuperscript{6} (Found: 175, Calc. 184.6), there seems to be considerable association and likelihood of this phospholanium chloride assuming a trigonal bipyramid geometry of the phosphorane which affects its tendency to form nitrilo-bisphosphonium chloride precursor to the cyclic and linear phosphazenes as postulated and isolated in several other cases. Further work is required before a definitive explanation can be given.

Characterization of aminocyclophosphazene from PCl\textsubscript{3}-NH\textsubscript{3}Cl-NH\textsubscript{3} reaction as octa-aminocyclootetraphosphazene is based on the P(N\textsubscript{3} ring vibration frequency observed as a broad IR band at 1220 cm\textsuperscript{-1}. We have carefully examined the IR spectrum of this product and found no absorption at 1170 cm\textsuperscript{-1} due to P\textsubscript{3}N\textsubscript{3} ring vibration reported by Audrieth and Sowerby\textsuperscript{7} in nujol mull for hexaaminocyclotriphosphazene. \textsuperscript{31}P NMR and molecular weight data would have readily ruled out the presence of hexa-aminocyclotriphosphazene as suggested by the referee. The IR spectral data are, however, conclusive to discard appreciable contamination by hexa-aminocyclotriphosphazene. As pointed out by the referee, the adduction of precursors of the cyclic and linear phosphazenes with hydrogen chloride may prevent polymerization and ring closure re-
actions in addition of reduction in the yield caused by the hydrolysis of the hydrogen chloride adducts during recrystallization. This would particularly be important in the PCl₅ reaction with NH₄Cl-NH₃ mixture where rapid condensation of phosphorus triamide (the aminolysis product) and possibility of hydrogen chloride addition of the complex species prior to chloramination could affect polymerization and ring closure reactions. In the case of 2-chloro-1,3-diazaphospholane, however, the well-known 1, 3 and 1, 4 side group-side group and side group-chain repulsions which introduce intramolecular repulsions and destabilizing influence in the phosphazene skeleton, can be a decisive factor in preventing self-condensation of the phospholanium chloride and hence polymerization and ring closure reactions.¹⁸

Experimental Procedure

Reagent grade solvents were dried over appropriate drying agents. Commercially available PCl₅ was refluxed under dry nitrogen purge to remove the dissolved hydrogen chloride, distilled and stored under dry nitrogen. The fraction distilling at 75.5°C was used. 2-Chloro-1,3,2-dioxaphospholane was prepared by a procedure described in literature (b.p. 49-51°C/19/mm; lit., b.p. 53-54°C/22-23 mm). 1,3-Dimethyl-2-chloro-1,3,2-diazaphospholane was prepared by the procedure of Scherer and Schmidt (b.p. 100-101°C/15-16 mm; lit., b.p. 98-100°C/14 mm). The PMR spectrum in CDCl₃ was consistent with a procedure described in literature. Prepared by a procedure described in literature®.

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Melting points were determined in Pyrex capillaries on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra in KBr were obtained on a Beckman IR-10 spectrophotometer. PMR spectra were recorded on a Varian model A 60-A instrument.

Reaction of PCl₅ with ammonia-chloramine mixture — A solution of PCl₅ (34.34 mmol) in dry benzene (200 ml) was prepared, chilled in ice-water and exposed for 1 hr to the gaseous effluents from chloramine generator. The resultant white solid was filtered, washed successively with benzene and ether and dried. The yield of 1.0 g after drying. A solution of this solid was prepared in 10 ml deionized water. After discarding the traces of insoluble matter, ethanol was added dropwise to the aqueous solution. The greasy white solid which settled at the bottom was separated from the milky white mother liquor by filtration and washed repeatedly with abs. ethanol to give octa-amino-cyclophosphazene as a white powder which after washing with ether was dried in vacuo for several hours, yield 0.3 g or 11.4% (based on PCl₅), decomposed near 200°C with evolution of ammonia (reported decomposition of octa-amino-cyclophosphazene, ~ 220°C (Found: N 54.24; P, 40.50. N₁₅P₄H₁₆ requires N, 54.54, P, 40.26%); IR : 3260(s), 3340(s), 1565(m), 1220(bs), 930(m). The white turbid mother liquor on chilling in the freezer yielded product which analyzed to an empirical composition NP(OH)(NH₃)₈, indicating hydrolysis of a substantial portion of the aminophosphazene derivative during recrystallization.

Reaction of 2-chloro-1,3,2-diazaphospholane with chloramine-ammonia mixture — The effluent gases from chloramine generator were bubbled through a solution of 2-chloro-1,3,2-dioxaphospholane (35.87 mmol) in dry benzene (60 ml) for 35 min and the reaction mixture cooled in ice-water. The white solid thus formed was filtered, washed with dry benzene and dried in vacuo. The solid, was treated with 100 ml freshly distilled diethylamine in 200 ml dry chloroform to remove ammonium chloride. The contents were refluxed under dry nitrogen until evolution of ammonia had ceased. The insoluble solid was filtered, washed with hot chloroform and dried in vacuo to give I (Found : C, 21.69; H, 4.73; N, 13.72; P, 26.86. C₈H₁₅N₃O₅P₂H₂O requires C, 21.62; H, 4.20; N, 12.61; P, 27.92%; IR: 3500-3100(bs), 1260(bs), 1040(s); reported in the literature for I, prepared by nucleophilic substitution of ethylene glycol on hexachlorocyclotriphosphazene, are 1250 (P₃N₃ ring vibrations)¹⁰ and 1040 cm⁻¹ (P-O-C aliphatic asymmetric stretching)¹¹.

Reaction of 1,3-dimethyl-2-chloro-1,3,2-diazaphospholane with chloramine-ammonia mixture — The effluent gases from chloramine generator were passed through a solution of 1,3-dimethyl-2-chloro-1,3,2-diazaphospholane (5.56 mmol) in dry benzene (75 ml) for 30 min and the reaction mixture cooled in ice-water. The white solid obtained was filtered, washed with benzene, dried in vacuo and freed from ammonium chloride by extraction with boiling chloroform. The greasy white residue remaining after evaporation of chloroform was boiled with 50 ml dry chloroform. The insoluble solid was filtered and dried (0.4 g), m.p. 171-77°C (Found : C, 25.93; H, 7.46; CI, 19.10; P, 16.62. C₆H₁₄N₃P₁Cl requires C, 26.01; H, 7.59; Cl, 19.24; P, 16.80%); PMR(DMSO-d₄) using sodium salt of 3-(trimethylsilyl)propanesulfonic acid as internal standard showed signals at 2.60 (d, 4H, JpCN = 3.17 (d, 4H, JpCN = 3.17 Hz), 5.48 (d, 4H, JpCN = 3.17 Hz), 5.48 Hz), 5.48 Hz). The combined yield of II including the fraction recovered from chloroform solution after precipitating with benzene was 1.01 g (83.46%). Compound II (0.45 g) was heated for 48 hr at 160-163°C in a vacuum sublimation apparatus at 1.5 × 10⁻⁵ torr. Analysis of the white sublimate by IR and PMR spectra showed it to be principally II with traces of ammonium chloride.

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References

5. UTVARY, K., Mh. Chem., 99 (1968), 1281; presumably the attempt to synthesize the spirotris(1,1,3,3,5,5,5,1,3-dimethyldiazacyclotriphosphazene) or higher homologs has been unsuccessful.