

tration range from 50 to ca. 53 mol % AlCl_3 in which it can be assumed that the variations in activity coefficients are negligible. At a composition almost identical with our AlCl_3 richest composition (i.e., at 53.6 mol % AlCl_3), vapor pressures of 27, 42, and 61 mmHg at 250, 275, and 300 °C, respectively, can be obtained from the diagram of Dewing.¹⁶ These values are somewhat higher than our values but agree however well with the vapor pressures of Viola et al.¹⁷ (at temperatures where the values can be compared).

It is obvious that model 2 can be neglected since it involves no uncharged species and could therefore only give rise to insignificant vapor pressures. Calculations using the pK values for models 1 and 3 from the potentiometric measurements and based on the assumption that the vapor pressure over the melt is proportional to the species fraction of Al_2Cl_6 in the melt (Raoult's law) are also shown in Table V. The vapor pressures of liquid Al_2Cl_6 necessary to make these calculations are from the work of Smits and Meijering.¹⁸ As discussed in connection with the vapor pressure measurements of KCl-AlCl_3 melts² there is no a priori reason to expect Raoult's law to be correct at low Al_2Cl_6 concentrations in the MCl-AlCl_3 systems ($M = \text{Li, Na, K, Rb, Cs}$), even though for the KCl-AlCl_3 system² it was found that calculations based on Raoult's law and Henry's law seemed to agree reasonably well. In the present case involving small vapor pressures, the measurements were

not accurate enough to use Henry's law. It was, however, found that the pressures calculated from Raoult's law with model 1 were 2-3 times higher than the measured vapor pressures, whereas the calculated vapor pressures with model 3 are much closer to the measured values.

It is clear that the uncertainties in the calculated vapor pressures for model 3 must be rather high. An idea of these uncertainties can be obtained by using the 95% nonlinear confidence ranges found for pK_4 (at 250 °C the calculated vapor pressure ranges are approximately from the measured vapor pressures to 50% above the measured vapor pressures, at 275 °C the ranges are approximately from 50% below to 30% above the measured vapor pressures, and at 300 °C the ranges are from 0 and up to the measured vapor pressures). However, the rather good agreement between the measured and calculated vapor pressures for model 3 at three different temperatures indicates that this may have a physical meaning (despite the uncertainties in these values and the use of Raoult's law) and that model 3 therefore gives the most realistic description of the reactions in acidic NaCl-AlCl_3 melts. This is as previously mentioned also in agreement with Raman spectra on MCl-AlCl_3 melts^{8,10} and with the results obtained on the KCl-AlCl_3 system.² Further potentiometric and vapor pressure measurements, especially at higher temperatures (and consequently at higher vapor pressures), but also on other MCl-AlCl_3 systems, should hopefully give information to prove or disprove the above ideas.

Acknowledgment. We gratefully acknowledge support from DANIDA for A.M. to collaborate in this work.

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Studies of Phosphazenes. 12.¹ Reactions of $\text{N}_4\text{P}_4\text{Cl}_8$ with Dibenzylamine. Isolation of an Unusual "Bicyclic" Phosphazene, $\text{N}_4\text{P}_4[\text{N}(\text{CH}_2\text{Ph})_2]_6(\text{NCH}_2\text{Ph})$

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Received March 4, 1981

Octachlorocyclotetraphosphazene, $\text{N}_4\text{P}_4\text{Cl}_8$, reacts with dibenzylamine to give the chloro(dibenzylamino) derivatives, $\text{N}_4\text{P}_4\text{Cl}_{8-n}[\text{N}(\text{CH}_2\text{Ph})_2]_n$, $n = 1, 2$ (two isomers), and 4 (three isomers). Nongeminal structures have been assigned to these compounds on the basis of ^1H and ^{31}P NMR spectra. The presence of at least two tris(dibenzylamino) derivatives in some reaction mixtures is also inferred from NMR spectra. Steric effects become important at the tetrakis stage of chlorine replacement, and further substitution by dibenzylamine to give monocyclic tetrameric derivatives does not occur. A "bicyclic" phosphazene, $\text{N}_4\text{P}_4[\text{N}(\text{CH}_2\text{Ph})_2]_6(\text{NCH}_2\text{Ph})$, is obtained from the reaction of $\text{N}_4\text{P}_4\text{Cl}_8$ with an excess of dibenzylamine in boiling methyl cyanide. The formation of this derivative and its spectroscopic data are discussed.

Introduction

Although numerous reactions of chlorocyclophosphazenes with amines have been investigated,⁴ the importance of steric effects in influencing the chlorine replacement pattern has not been evaluated in any detail. Reactions of hexachlorocyclotriphosphazene, $\text{N}_3\text{P}_3\text{Cl}_6$, with the bulky reagents dibenzylamine,⁵ dicyclohexylamine,⁶ and P,P,P -triphenylmonophosphazene, $\text{HN}=\text{PPh}_3$,⁷ terminate at the bis stage of chlorine replacement, an observation that has been attributed mainly to steric factors. It is of interest to study the reaction

of a sterically demanding nucleophile with the more reactive homologue^{4,8} octachlorocyclotetraphosphazene, $\text{N}_4\text{P}_4\text{Cl}_8$ (I). In this paper, the results of a systematic investigation of the reaction between $\text{N}_4\text{P}_4\text{Cl}_8$ (I) and dibenzylamine are reported. In addition to several chloro(dibenzylamino)cyclotetraphosphazenes, an unusual "bicyclic" phosphazene is formed.⁹ The distinctive spectroscopic features of the latter are highlighted.

Results and Discussions

Chloro(dibenzylamino)cyclotetraphosphazenes and the Chlorine Replacement Pattern. The chloro(dibenzylamino) derivatives, $\text{N}_4\text{P}_4\text{Cl}_{8-n}[\text{N}(\text{CH}_2\text{Ph})_2]_n$ (II-VII), isolated from the reaction of dibenzylamine with the octachloride (I) possess nongeminal disposition of the dibenzylamino substituents (Figure 1). The structural assignments for these compounds

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(4) S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Adv. Inorg. Radiochem.*, **21**, 41 (1978).

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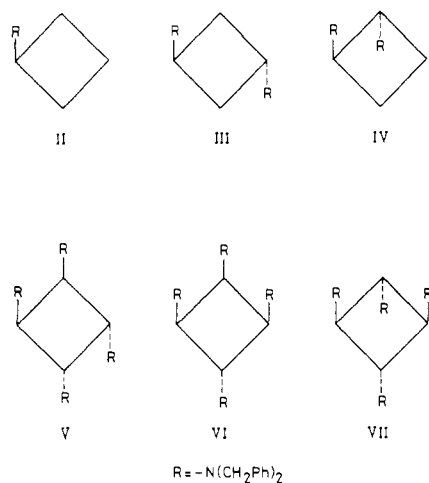


Figure 1. Structures of chloro(dibenzylamino) derivatives, N₄P₄Cl_{8-n}R_n (II–VII). The corners of the square represent phosphorus atoms; ring nitrogen and chlorine atoms not shown.

follow from their ¹H and ³¹P NMR spectroscopic data (Experimental Section).^{4,5,10} In most spectra, the CH₂ doublet showed intense “virtual coupling”.^{4,10} The ³¹P NMR spectrum of the crystalline bis isomer N₄P₄Cl₆[N(CH₂Ph)₂]₂ (III) consists of only three lines (centered at δ -3.9) indicating the closeness of the chemical shifts of ≡PCl₂ and ≡PCl(R) groups. However, the ³¹P NMR spectra of its methoxy and trifluoroethoxy derivatives, N₄P₄[N(CH₂Ph)₂]₂(OMe)₆ (IX) and N₄P₄[N(CH₂Ph)₂]₂(OCH₂CF₃)₆ (X), are clearly of the A₂B₂ type and confirm the 2,6-structure of the chloro precursor (III). The ¹H NMR spectrum of the methoxy derivative, N₄P₄[N(CH₂Ph)₂]₂(OMe)₆ (IX), shows two OMe doublets in the intensity ratio 2:1, thus establishing the 2-trans-6 disposition of the dibenzylamino substituents. The ³¹P NMR spectrum of the other bis isomer IV is a symmetrical pattern of the AA′BB′ type which suggests a 2,4-arrangement of dibenzylamino groups.¹¹ The experimental spectrum and that obtained by computer simulation are depicted in Figure 2.¹³ The structural assignments for the tetrakis(dibenzylamino) isomers (V and VII)¹⁴ are somewhat tentative and are based on their relative TLC R_f values.¹⁰ In addition to these pure compounds, two substances of composition N₄P₄Cl₅[N(CH₂Ph)₂]₃ (mass spectral evidence) have been isolated (see Table I). They are mixtures of tris(dibenzylamino) derivatives as shown by their ¹H and ³¹P NMR spectra. The ¹H NMR data also suggest that the substance having a TLC R_f value of 0.57 [benzene-petroleum ether (1:3)] consists of nongeminal tris isomers only [³J(P–H) = 14.0–15.0 Hz].

The results thus show that the replacement of chlorine atoms from the octachloride I by the dibenzylamino substituent proceeds predominantly by a nongeminal pathway.

Isolation and Characterization of the Novel “Bicyclic” Phosphazene N₄P₄[N(CH₂Ph)₂]₆(NCH₂Ph) (VIII). The most

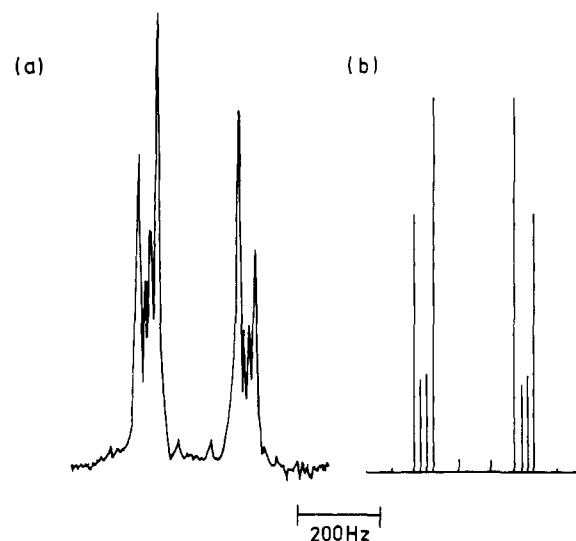


Figure 2. Phosphorus-31 NMR spectrum of 2,4-N₄P₄Cl₆[N(CH₂Ph)₂]₂ (IV): (a) experimental spectrum; (b) simulated spectrum using LAOCOON 3 program. The parameters are: δ_{PCl₂} -6.8 (A), δ_{PCIN(CH₂Ph)₂} -0.2 (B); ²J(A–A′) = 36.9 Hz, ²J(A–B) = 38.1 Hz, ²J(B–B′) = 40.0 Hz, ⁴J(A–B′) = -1.0 Hz.

interesting aspect of the present study is the isolation of a novel “bicyclic” compound, N₄P₄[N(CH₂Ph)₂]₆(NCH₂Ph) (VIII), from the reaction of the octachloride I with an excess of dibenzylamine in boiling methyl cyanide (yield 3.5%). Elemental analysis indicates the formula C₉₁H₉₁N₁₁P₄, and this is confirmed by mass spectrometry; intense peaks at 1460.6330, 1370.5880, and 1278.5220, attributable to [M – H]⁺ (*m/e* calcd, 1460.6330), [M – CH₂Ph]⁺ (*m/e* calcd, 1370.5861), and [M – (CH₂Ph)₂]⁺ (*m/e* calcd, 1278.5235) are observed. A peak is also observed at *m/e* 639.5 which is probably due to the doubly charged species [M – (CH₂Ph)₂]²⁺.

The 270-MHz ¹H NMR spectrum of compound VIII consists of a triplet and three doublets in the NCH₂ region (intensity ratio 1:2:2:2). The spectrum and assignments are shown in Figure 3. A noteworthy observation is the appearance of the [=N(9)CH₂] triplet at relatively high δ (low field). For the “bicyclic” phosphazenes reported previously,^{16–18} the =N(9)R signal always appears upfield from the resonance(s) of the groups attached to the junction phosphorus atoms [P(2) and P(6)].¹⁹ The considerable deshielding of the =N(9)CH₂ protons observed for the “bicyclic” compound VIII is probably because of the aromatic ring current effect although electronic effect could also be a contributing factor.^{16,18} An A₂B₂-type ³¹P {¹H} NMR spectrum is expected for this “bicyclic” compound; only a symmetrical triplet centered at ca. δ 21 is observed owing to the accidental proximity of the chemical shifts of P(2),P(6) and P(4),P(8) pairs of nuclei. The phosphorus-31 chemical shift is characteristic of a bicyclic phosphazene^{16–18} and is well separated from the region (δ +2.0 to -6.0) associated with the chloro-(dibenzylamino)cyclotetraphosphazenes II–VII.

The infrared spectrum of the bicyclic compound VIII is shown in Figure 4(a). A strong doublet centered at 1180 cm⁻¹ and another strong and sharp band at 790 cm⁻¹ are prominent

- (10) S. S. Krishnamurthy, M. N. Sudheendra Rao, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *Inorg. Chem.*, **17**, 1527 (1978).
- (11) X-ray crystallography reveals that one of the two bis(*N*-methyl-anilino)hexachlorocyclotetraphosphazenes isolated in an earlier study¹⁰ possesses the 2-trans-4 structure.¹² It seems probable that isomer IV will also have this structure.
- (12) Y. Sudhakar Babu and H. Manohar, *Cryst. Struct. Commun.*, **6**, 803 (1977).
- (13) The enhanced intensity of the low-field half of the spectrum is due to nuclear Overhauser effect and supports the assignments indicated in Figure 2.
- (14) The all-cis structure is excluded owing to the steric requirements of four bulky dibenzylamino groups. A compound with the all-cis structure is not formed in the reactions of the octachloride (I) with dimethylamine¹⁵ or *N*-methylaniline.¹⁰
- (15) D. Millington and D. B. Sowerby, *J. Chem. Soc., Dalton Trans.*, 2035 (1972).

- (16) S. S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. A. Shaw, M. Woods, and R. Keat, *J. Chem. Res., Synop.*, **70** (1977); *J. Chem. Res., Miniprint*, 0860–0884 (1977).
- (17) S. S. Krishnamurthy, K. Ramachandran, A. C. Sau, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *Inorg. Chem.*, **18**, 2010 (1979).
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- (19) The N(9) methyl protons of the “bicyclic” phosphazene hydrochloride adduct N₄P₄(NHMe)₆(NMe)·HCl are also deshielded compared to those of the junction phosphorus atoms, but in this case the result is attributed to protonation at the bridgehead nitrogen atom, N(9).¹⁸

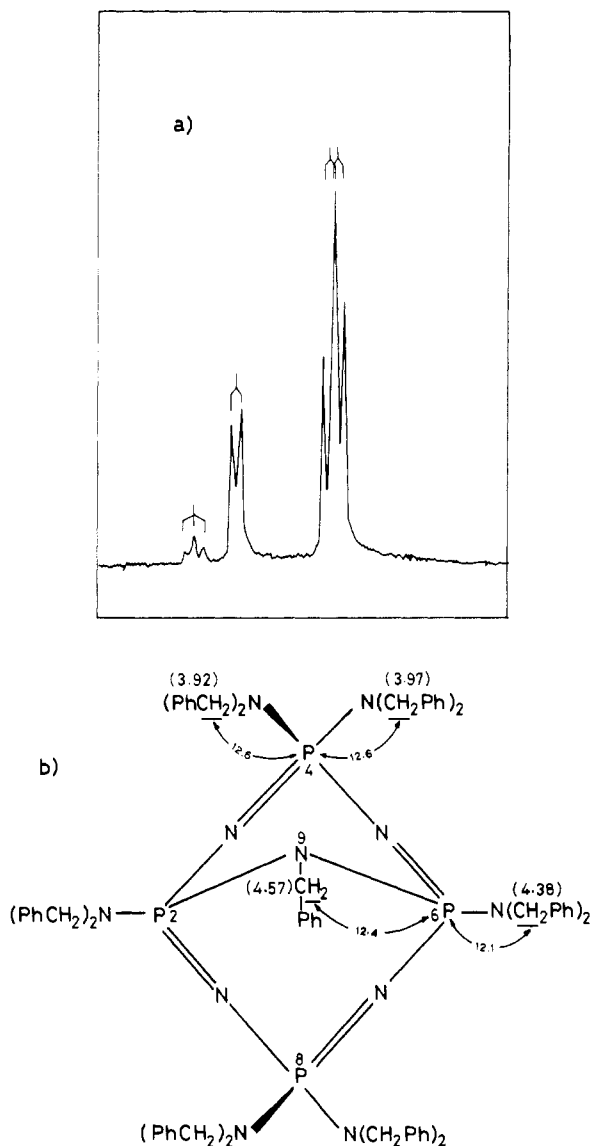


Figure 3. (a) The 270-MHz proton NMR spectrum of the "bicyclic" phosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (VIII). (b) The assignments. Values shown in parentheses indicate chemical shifts; those enclosed between curved arrows indicate the phosphorus-proton spin coupling constants [$^3J(P-H)$].

but are absent in the spectra of chloro(dibenzylamino)cyclo-tetraphosphazene derivatives (see Figure 4(b) for a typical spectrum). These bands are assigned to $\nu(P=N)$ and to the bridging $P(2)-N(9)-P(6)$ unit—the phosphazane part of the bicyclic skeleton.¹⁸ The ring $P=N$ stretching frequency ($1300-1310\text{ cm}^{-1}$) for the chloro(dibenzylamino)cyclo-tetraphosphazenes II-VII does not vary significantly with increasing degree of aminolysis. This observation may be contrasted with the usual decrease in $\nu(P=N)$ with increasing degree of chlorine replacement by amino groups (e.g., NHMe, NHEt, NMe₂).⁴ The possible reasons for the negligible variation in $\nu(P=N)$ for the dibenzylamino derivatives II-VII are (a) the weak electron-releasing character of the dibenzylamino groups and (b) steric effects which prevent the exocyclic substituent from adopting a planar configuration necessary for effective exocyclic π bonding.²⁰

Mechanism of Formation of the "Bicyclic" Phosphazene VIII. The syntheses of "bicyclic" phosphazenes from the reactions of the octachloride I with methylamine¹⁸ and ethylamine¹⁶ and those of 2-*trans*-6-bis(primary alkylamino)-

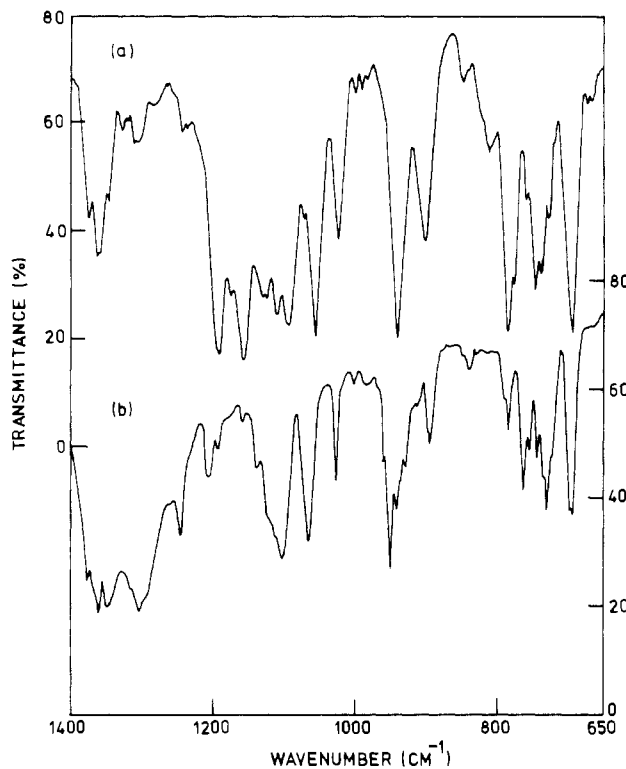


Figure 4. IR spectrum (Nujol mull) of (a) $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (VIII) and (b) 2,4,6,8- $N_4P_4Cl_4[N(CH_2Ph)_2]_4$ (V).

hexachlorocyclo-tetraphosphazenes with dimethylamine¹⁷ have been described previously. A proton abstraction mechanism has been postulated for the intramolecular trans-annular nucleophilic substitution reaction. The formation of the "bicyclic" dibenzylamino compound VIII isolated in the present study presumably involves a dealkylation step prior to or concomitant with the intramolecular nucleophilic attack.²¹ Dealkylation of secondary amines in the presence of hydrogen halides has been observed in several organic reactions.²² Such dealkylations apparently occur more readily in the presence of phosphorus(V) chlorides^{23,24} and chlorocyclophosphazenes.^{23,25} For example, Healy et al. have noted that in the reaction of phenyl phosphonothioic dichloride, $PhP(S)Cl_2$, with dibenzylamine in benzene or chloroform, dealkylation occurs under mild conditions ($\sim 25^\circ\text{C}$) to yield a mixed benzylamino-dibenzylamino derivative, $PhP(S)[N(CH_2Ph)_2](NHCH_2Ph)$.²⁴

Steric Effect in the Aminolysis Reactions of Chlorocyclophosphazenes. It is worthwhile to compare the reactions of the oligomeric chlorocyclophosphazenes $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with dibenzylamine. In the $N_3P_3Cl_6$ system, substitution does not exceed the bis stage even under very drastic experimental conditions ($>150^\circ\text{C}$, sealed tubes). Complete replacement of the four chlorine atoms of the bis compound $N_3P_3Cl_4[N(CH_2Ph)_2]_2$ by methoxide proceeds easily in boiling benzene whereas the reaction with dimethylamine results only in the

- (21) There is evidence to suggest that the trans-annular attack to yield "bicyclic" phosphazenes in the reaction of (primary amino)chlorocyclo-tetraphosphazenes with amines occurs only after the bis stage of chlorine replacement.¹⁷
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Table I. Preparative Details^a

amt of N ₄ P ₄ Cl ₈ (I)		amt of dibenzylamine		solvent (V, cm ³)	react t, h	products and yields		
g	mmol	g	mmol			no.	g	%
9.28	20	7.88	40	CH ₃ CN (250) ^b	2.5	II	5.50	40.5
						III	0.25	2.0
						II + III + IV ^c	1.00	
2.32	5	1.97	10	CH ₃ CN (65)	2.0	II	0.50	16.0
						II + III + IV ^c	1.00	
2.32	5	3.94	20	CH ₃ CN (110) ^d	4.5	II	0.10	4.0
						III	1.15	30.0
						IV	0.70 ^e	19.0
						II + III + IV ^c	1.15	
2.32	5	3.94	20	CHCl ₃ (80)	9.5	II	0.52	16.00
						III	0.36	9.2
						IV	0.50	13.6
						III + IV ^c	0.40	
						III	0.30	7.6
2.32	5	5.91	30	CH ₃ CN (135)	8.5	IV ^f	0.05	1.3
2.32	5	7.88	40	CH ₃ CN (150) ^d	15.0	V	0.25	4.5
						VII ^g	0.30	5.5

^a Reactions carried out in boiling solvent. ^b Reaction carried out at ~25 °C. ^c Obtained as mixture after column chromatography.

^d Reaction was also carried out in toluene (130 cm³, 7 h for 1:4; 150 cm³, 24 h for 1:8 stoichiometry). TLC of the reaction mixtures showed the same degree of complexity as observed with CH₃CN. ^e 0.30 g of a mixture of N₄P₄Cl_{8-n}[N(CH₂Ph)₂]_n with lower R_f values was also obtained. ^f Two oily liquids of composition N₄P₄Cl₂[N(CH₂Ph)₂]₃, R_f 0.57 [benzene-petroleum ether (1:3)] and R_f 0.41 [benzene-petroleum ether (2:3)] were also isolated (yields 21% and 6%, respectively); in addition, 0.08 g of a mixture of derivatives with lower R_f values was obtained. ^g 0.15 g of N₄P₄Cl₃[N(CH₂Ph)₂]₃ (R_f 0.57—see f) and 0.30 g of a mixture of derivatives with lower R_f values were also obtained.

formation of N₃P₃Cl₂[N(CH₂Ph)₂]₂(NMe₂)₂.⁵ The reaction of the octachloride I with dibenzylamine yields a complex mixture of products, and a nongeminal mode of chlorine replacement is established. The "steric effect" assumes importance only after the tetrakis stage of chlorine replacement, and further substitution by dibenzylamine to give monocyclic tetrameric derivatives apparently does not occur. However, complete replacement of the chlorine atoms of the 2-*trans*-6-bis(dibenzylamino) derivative III by OMe or OCH₂CF₃ groups is readily achieved (see Experimental Section).

In the light of the above observations, the formation of the bicyclic compound VIII containing six bulky dibenzylamino groups is unusual and unexpected. The apparent paradox can be rationalized by a consideration of the molecular geometry of bicyclic phosphazenes.²⁶ Their molecular skeletons resemble that of adamantane, with the bridge nitrogen projecting well above the two puckered P-N ring segments. The bridge nitrogen atom has a pyramidal configuration, and the P-N bonds at this nitrogen atom are longer (1.71–1.76 Å) than the other skeletal P-N bonds (1.58–1.61 Å). This type of structure can accommodate the bulky groups better than a simple eight-membered cyclotetraphosphazene ring. The "steric effect" is probably the driving force for the dealkylation step and the subsequent formation of the P-N(R)-P bridge. An investigation of the reactions of N₄P₄Cl₆(NHEt)₂ with bulky secondary amines—pyrrolidine, diethylamine, and piperidine—shows that the bicyclic phosphazenes are more readily formed than the fully aminolyzed cyclotetraphosphazenes N₄P₄(NR₂)₆(NHEt)₂.²⁷ This result again reflects the different steric constraints of the cyclotetraphosphazene and the related bicyclic ring skeletons.

Conclusion

Three major pathways¹⁷ have been identified in the aminolysis reactions of the octachloride I and its bis(alkylamino) derivatives (N₄P₄Cl₆(NHR)₂): (a) stepwise replacement of chlorine atoms to give partially and fully substituted cyclotetraphosphazenes, (b) intermolecular condensation yielding

resins, and (c) an intramolecular nucleophilic reaction leading to the formation of "bicyclic" phosphazenes. We may now add a fourth process, viz., dealkylation-cum-trans-annular attack, which could well be a feature of the reactions of the octachloride I with bulky secondary amines.

Experimental Section

Octachlorocyclotetraphosphazetetrane (I) was purified by recrystallization from petroleum ether (bp 60–80 °C) to a constant melting point of 124 °C. Petroleum ether (bp 40–60 °C, unless stated otherwise), aromatic hydrocarbons, chloroform, and methyl cyanide were purified by conventional methods. Dibenzylamine (SD'S Lab-Chem. Industry, Bombay, India) was distilled [113 °C (2 mm)] before use. Trifluoroethanol was obtained from Fluka, Switzerland. Silica gel for thin-layer and column chromatography was supplied by BDH, U.K. In general, 25–30 g of silica gel was required to separate 1 g of reaction mixture.

Proton NMR spectra (CDCl₃ solution, Me₄Si internal standard) were recorded with Jeol MH 100, Varian HR 220, and Bruker WH 270 spectrometers. ³¹P {¹H} NMR spectra were obtained from a Bruker WH 90 spectrometer using CDCl₃ solutions and 85% phosphoric acid as an external standard. Chemical shifts are expressed on the δ scale with upfield shifts negative. The IR spectra were obtained in Nujol mulls by using Carl Zeiss UR 10 and Perkin-Elmer 457 spectrometers. Mass spectrometric data were obtained from an AEI MS 902 spectrometer (PCMU Service, Harwell, U.K.). Melting points are uncorrected and were determined with a Reichert-Kofler Microheating stage fitted with a polarizing microscope. A Varian aerograph series 1800 was used for the qualitative GLC experiments. A steel column (20 × 1/4 in.) containing OV 25 10% on 60/80N AW DMCS was used. Column temperatures were 225–240 °C.

Preparative Details. Reactions of N₄P₄Cl₈ (I) with dibenzylamine were carried out in different organic solvents using various relative preparations of reactants. Each reaction gave a complex mixture of products, and extensive column chromatography was essential in most cases to obtain pure compounds. Many fractions were obtained which were mixtures even though they showed a single spot in TLC. Gas-liquid chromatographic analyses of the reaction mixtures were attempted using trifluoroethoxy derivatives.²⁸ The product from

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(27) S. R. Contractor, S. S. Krishnamurthy, P. Ramabrahmam, R. A. Shaw, A. R. Vasudeva Murthy, and M. Woods, unpublished results.

(28) This "derivatization" technique increases the volatility of cyclotetraphosphazenes²⁹ and minimizes their thermal decomposition at the high column temperatures (200–250 °C) which are usually employed for the GLC separation of (amino)chlorocyclotetraphosphazenes.^{15,30}

(29) J. L. Schmutz and H. R. Allcock, *Inorg. Chem.*, **14**, 2433 (1975).

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"exhaustive trifluoroethoxylation" of 1:6 stoichiometric and excess $N_4P_4Cl_8$ -dibenzylamine reaction mixtures gave essentially the same type of GLC traces (3-4 major peaks having retention times 20-60 min at 220 °C) in addition to broad asymmetric peaks with longer retention times. Definite evidence could not be obtained for the precise number and nature of the components present.

The general experimental procedure has been described previously.¹⁰ The preparation of the bicyclic derivative $N_4P_4[N(CH_2Ph)_2]_6N(CH_2Ph)$ (VIII) is described below and details of other reactions are summarized in Table I. The following pure compounds were isolated. $N_4P_4Cl_7[N(CH_2Ph)_2]$ (II): mp 109-110 °C; R_f [TLC (silica gel; eluant benzene-petroleum ether (1:3))] 0.86; 1H NMR [δ_{CH_2} with $^3J^*(P-H)$ in parenthesis] 4.20 (14.0 Hz); ^{31}P NMR complex multiplet δ -6.0; IR $\nu(P=N)$ 1300 cm^{-1} . Anal. Calcd for $C_{14}H_{14}Cl_7N_5P_4$: C, 26.9; H, 2.3; N, 11.2. Found: C, 27.6; H, 2.7; N, 10.6. $N_4P_4Cl_6[N(CH_2Ph)_2]_2$ (III): mp 156-158 °C; R_f 0.80; 1H NMR 4.12 (14.8 Hz); ^{31}P NMR symmetrical triplet centered at δ -3.9 (A_2B_2 tending to A_4); IR $\nu(P=N)$ 1310 cm^{-1} . Anal. Calcd for $C_{28}H_{28}Cl_6N_6P_4$: C, 42.8; H, 3.6; N, 10.7. Found: C, 42.8; H, 3.7; N, 10.5. $N_4P_4Cl_6[N(CH_2Ph)_2]_2$ (IV): waxy solid; R_f 0.76; 1H NMR 4.24 (15.5 Hz); ^{31}P NMR, see Figure 2; IR $\nu(P=N)$ 1315 cm^{-1} . Anal. Found: C, 42.9; H, 3.9; mass spectrum m/e (obsd) 784 ($C_{28}H_{28}^{35}Cl_5^{37}N_6P_4$)⁺, 691 ($M - CH_2Ph$)⁺, 654 ($M - (CH_2Ph) - Cl$)⁺. $N_4P_4Cl_4[N(CH_2Ph)_2]_4$ (V): mp 114-115 °C; R_f [eluant benzene-petroleum ether (2:3)] 0.69; 1H NMR 4.27 (14.0 Hz); ^{31}P NMR 2.22; IR $\nu(P=N)$ 1300 cm^{-1} . Anal. Calcd for $C_{56}H_{56}Cl_4N_8P_4$: C, 60.8; H, 5.1; N, 10.1. Found: C, 61.4; H, 5.2; N, 10.2. $N_4P_4Cl_4[N(CH_2Ph)_2]_4$ (VI): waxy solid; R_f 0.53; 1H NMR (220 MHz) 4.15 (14.0 Hz), 4.34 (15.0 Hz), 4.40 (15.0 Hz); ^{31}P NMR δ 1.98. Anal. Found: C, 60.3; H, 6.0; N, 10.6. $N_4P_4Cl_4[N(CH_2Ph)_2]_4$ (VII): mp 93-95 °C; R_f 0.53; 1H NMR 4.29 (13.6 Hz); ^{31}P NMR δ 2.01; IR $\nu(P=N)$ 1300 cm^{-1} . Mass spectrum m/e (obsd) 1104.2360 [M^+ requires 1104.2332], 1069.2650 ($M - Cl$)⁺, 1013.1795 ($M - CH_2Ph$)⁺. $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (VIII): mp 252-254 °C; R_f 0.83 [eluant benzene-petroleum ether (1:1)]; ^{31}P NMR symmetrical triplet centered at δ 21.3 (A_2B_2 tending to A_4); IR $\nu(P=N)$ 1180 cm^{-1} , $\nu[P(2)-N(9)-P(6)]$ 790 cm^{-1} . (Anal., see below.) $N_4P_4(OMe)_6[N(CH_2Ph)_2]_2$ (IX): liquid; 1H NMR δ_{CH_2} 4.17 (11.0 Hz), δ_{OCH_3} 3.55 (12.5), 3.50 (12.0) ratio 1:2; ^{31}P NMR $\delta_{P(OMe)_2}$ 1.5, $\delta_{P(OMe)[N(CH_2Ph)_2]}$ -4.0, $^2J(P-P) = 65.0$ Hz. $N_4P_4(OCH_2CF_3)_6[N(CH_2Ph)_2]_2$ (X): liquid; 1H NMR $\delta_{C_6H_5}$ 7.25, δ_{NCH_2/OCH_2} 4.1; ^{31}P NMR $\delta_{P(OCH_2CF_3)_2}$ 5.9, $\delta_{P(OCH_2CF_3)[N(CH_2Ph)_2]}$ -3.6, $^2J(P-P)$ 67.0 Hz. Compounds IX and X were prepared in 70% yield by heating compound III with sodium alkoxide in boiling tetrahydrofuran (96 h). The compounds were GLC pure and further

characterized by ^{31}P NMR (A_2B_2 patterns) and 1H NMR spectroscopy.

Preparation of the "Bicyclic" Derivative, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (VIII). Dibenzylamine (30.0 g, 150 mmol) was added to a stirred solution of $N_4P_4Cl_8$ (I) (2.32 g, 5 mmol) in methyl cyanide at 80 °C. After 160 h, the solvent and unreacted dibenzylamine were distilled under reduced pressure. The sticky residue was heated under reflux with activated charcoal in benzene-petroleum ether (1:1), and the solution was filtered. TLC [eluant benzene-petroleum ether (2:3)] of the filtrate showed that at least six compounds were present. The mixture (4.50 g) was subjected to column chromatographic separation [silica gel (125 g)], and three main fractions (A-C) were collected. Elution with benzene-petroleum ether (2:3) gave fractions A (0.30 g) and B (0.25 g). Fraction A was identified as 2,4,6,8-tetrachlorotetrakis(dibenzylamino)cyclotetraphosphazene (VI); fraction B was an oil, and TLC, elemental analysis, and ^{31}P NMR (complex spectrum from +7 to -6 ppm) suggested a mixture of two (or possibly three) additional tetrakis derivatives. Elution with benzene-petroleum ether (1:1) gave fraction C (0.25 g), which on evaporation of the solvent yielded a sticky solid. After several recrystallizations from methylene chloride-petroleum ether (1:1), the bicyclic derivative, 2,4,4,6,8,8-hexakis(dibenzylamino)-9-benzyl-2,6-epiminocyclotetraphosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$ (VIII) (mp 252-254 °C), was obtained. (Anal. Calcd for $C_{91}H_{91}N_{11}P_4$: C, 74.7; H, 6.3; N, 10.3. Found: C, 74.3; H, 6.3; N, 10.3.) Elution with benzene gave several minor fractions, but pure compounds could not be obtained from these oily residues. Analytical data for two of these residues clearly showed that chlorine replacement had not exceeded the tetrakis stage. Anal. Calcd for $C_{56}H_{56}Cl_4N_8P_4$: C, 60.78; H, 5.10; N, 10.10. (i) Found: C, 58.48; H, 5.25; N, 8.45. (ii) Found: C, 57.04; H, 5.28; N, 8.81. The 1H and ^{31}P NMR spectra of these substances show they are mixtures of (chlorodibenzylamino)cyclotetraphosphazene derivatives.

Acknowledgment. The authors thank the University Grants Commission, New Delhi, and the Overseas Development Administration, U.K., for support and Professors A. R. Vasudeva Murthy and R. A. Shaw for their interest. Our thanks are also due to Dr. K. S. Dhathathreyan for assistance in computer simulation.

Registry No. I, 2950-45-0; II, 79448-98-9; III, 79448-99-0; IV, 79449-00-6; V, 79449-01-7; VI, 79516-85-1; VII, 76816-86-2; VIII, 76312-46-4; IX, 79449-02-8; X, 79449-03-9; $N_4P_4Cl_5[N(CH_2Ph)_2]_3$, 79449-04-0; dibenzylamine, 103-49-1.

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The Reaction between Sulfur Dioxide and Hexamethyldisilazane. 2. Oxygen Atom Transfer from Sulfur Dioxide

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Received July 16, 1981

The new reaction between sulfur dioxide and hexamethyldisilazane, which forms $((CH_3)_3Si)_2O$, $(CH_3)_3SiNSO$, and $NH_4(CH_3)_3SiOSO_2$, is characterized. In this reaction oxygen is transferred to silicon and sulfur from sulfur dioxide, but Si-N bonding is still partially retained. The solid product, ammonium trimethylsilyl sulfite, sublimes readily at ambient temperature but exhibits ionic properties. The variety of products and the overall reaction stoichiometry impose severe restrictions on possible reaction mechanisms. These constraints are discussed, and a consistent reaction scheme is proposed for this facile but unusual reaction.

Introduction

Many amines react with sulfur dioxide to yield stable one-to-one products. In such cases an acid-base adduct is generally proposed as the species initially formed, with the

adduct either retaining its donor-acceptor structure¹ (e.g., $(CH_3)_3N + SO_2 \rightarrow (CH_3)_3N \cdot SO_2$) or rearranging to form a stable compound in which the proton bound to nitrogen migrates to oxygen (eq 1).² In a few instances the rearrangement products have been observed to result in cleavage of SO_2 and

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