Indian Journal of Chemistry
Vol. 22A, January 1983, pp. 1-5

Studies of Phosphazenes: Part 16†—Spectroscopic Investigations of Bicyclic Phosphazenes of Types $N_4P_4(NHR)_6(NR)$ & $N_4P_4(NMe_2)_5(NHR')(NR)$

P RAMABRAHMAM, K S DHATHATHREYAN & S S KRISHNAMURTHY*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012
and
MICHAEL WOODS
Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX, UK

Received 2 *September* 1982; *accepted* 27 *September* 1982

Octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) reacts with an excess of *n*-propylamine, isopropylamine or *n*-butylamine in chloroform to give a mixture of bicyclic phosphazene, $N_4P_4(NHR)_6(NR)$, and octakis(amino) derivative, $N_4P_4(NHR)_8$. The bicyclic phosphazenes are only formed in low yields when R = Pr^i, Bu^n; formation of bicyclic phosphazene has not been detected in the reaction of $N_4P_4Cl_8$ with benzylamine. Characteristic spectroscopic features (^{31}P NMR and IR) of the products are presented. Phosphorus-31 NMR parameters for six asymmetrically substituted bicyclic phosphazenes, $N_4P_4(NMe_2)_5(NHR')(NR')$, have been obtained by computer analysis and these results are also discussed.

Reactions of octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) with primary amines have been reported only recently[1,2]. Chloro-(amino) derivatives are obtained (Eq. 1) and the derivatives have nongeminal structures ($\equiv PCl.NHR$ and $\equiv PCl_2$ groups only).

$$N_4P_4Cl_8 + 2nRNH_2 \rightarrow N_4P_4Cl_{8-n}(NHR)_n + nRNH_2.HCl \quad \ldots(1)$$

R = Et; n = 1, 2 (two isomers), 3, 4 (two isomers), 8; R = Bu^t; n = 1, 2 (two isomers), 3, 8.

Intermolecular condensation reactions[3] also occur but they can be partially suppressed by using an excess of primary amine[1,2]. A third reaction pathway is observed when $N_4P_4Cl_8$ reacts with an excess of methylamine[4] or ethylamine[5] in chloroform to give bicyclic phosphazenes, $N_4P_4(NHR)_6(NR)$. In the present study, the reactions of other primary amines with $N_4P_4Cl_8$ have been explored in order to assess the possible role of the nucleophile on the formation of bicyclic phosphazenes. In addition, ^{31}P NMR data for the bicyclic phosphazenes, $N_4P_4(NMe_2)_5(NHR')(NR)$, obtained by computer analysis are given and compared with those obtained for the symmetrically substituted analogues, $N_4P_4(NHR)_6(NR)$.

The yields of octakis(amino) derivatives, $N_4P_4(NHR)_8$, and bicyclic phosphazenes, $N_4P_4(NHR)_6(NR)$, formed in the reaction of the tetrameric chloride, $N_4P_4Cl_8$, with an excess of primary amine, RNH_2(R = Pr^n, Pr^i, Bu^n) in chloroform/triethylamine are given in Table 1. Similar data obtained earlier for the analogous reactions involving methylamine[4] and ethylamine[5] are also included but it should be noted that the yields of products are considerably decreased owing to the competitive formation of non-crystalline resins. In contrast, the amount of resinous material detected in the present study is negligible. Presumably intermolecular condensation reactions[3] are considerably retarded as the bulkiness of the nucleophile and/or the amino substituent increases, albeit only if an excess of amine is used[1,2].

Table 1—Reactions of $N_4P_4Cl_8$ with an Excess of Primary Amine (RNH_2) in Chloroform[a]

[In the reaction with *n*-Pr NH_2, *i*-Pr NH_2 and *n*-BuNH_2, Et_3N was also added]

R	yield (%) of	
	Bicyclic phosphazene [$N_4P_4(NHR)_6(NR)$]	Octakis(amino)-cyclotetraphosphazene [$N_4P_4(NHR)_8$]
Me	16[b]	35[b]
Et	35[c]	2[c]
Pr^n	60	22
Pr^i	11	70
Bu^n	16	60
$PhCH_2$	0	63[d]

(a) Yields estimated from phosphorus-31 NMR data
(b) Amount of product isolated[4] (yield of bicyclic phosphazene includes 8% of its hydrochloride adduct). Resin also formed.
(c) Amount of product isolated[5] (yield of bicyclic phosphazene includes 33% of its hydrochloride adduct). Resin also formed.
(d) Pure product.

† Part 15: Dhathathreyan K S, Krishnamurthy S S & Woods M M, *J Chem Soc Dalton Trans* (in press).

The formation of the bicyclic phosphazene, $N_4P_4(NHR)_6(NR)$, varies according to the nature of the organic group R. The yield of the bicyclic product increases in the order: $Pr^i < Me \approx Bu^n < Et < Pr^n$. Formation of bicyclic phosphazene is not observed in the reaction of $N_4P_4Cl_8$ with benzylamine in chloroform: the octakis (benzylamino) derivative, $N_4P_4(NHCH_2Ph)_8$, is the sole product (^{31}P NMR evidence). An intramolecular *trans*-annular nucleophilic substitution, which initially involves at least one proton abstraction step[6], is suggested for the formation of bicyclic phosphazenes. The steady increase in their yields in the series, $Me < Et < Pr^n$, may indicate that the electron releasing power of the alkyl group plays a significant role in promoting the proton abstraction step. The electronic and steric requirements of *n*-propylamine are clearly most favourable for the formation of a bicyclic phosphazene. A further increase in the carbon chain length (*n*-butylamine) is accompanied by a sharp decrease in the yield of the bicyclic product. This trend is also very clear in dimethylaminolysis reactions of 2-*trans*-6-bis(alkylamino)-cyclotetraphosphazenes, $N_4P_4(NHR)_2Cl_6$ (R = Me, Et, Pr^n, Bu^n) which lead to the formation of the asymmetrically substituted, bicyclic phosphazenes, $N_4P_4(NMe_2)_5(NHR)(NR)$[6].

Two other observations are worthy of comment. The absence of the bicyclic product $N_4P_4(NHCH_2Ph)_6$-(NCH_2Ph) in the reaction of benzylamine with $N_4P_4Cl_8$ may be contrasted with the ready formation of the bicyclic phosphazene, $N_4P_4(NMe_2)_5(NHCH_2Ph)(NCH_2Ph)$ (40% yield), in the reaction of $N_4P_4(NHCH_2Ph)_2Cl_6$ with an excess of dimethylamine in chloroform[6]. On the other hand, isopropylamine behaves in the opposite fashion: the bicyclic phosphazene, $N_4P_4(NHPr^i)_6(NPr^i)$ is formed (albeit in only modest quantity) whereas $N_4P_4(NHPr^i)_2Cl_6$ reacts with an excess of dimethylamine in chloroform[6] to give only the cyclotetraphosphazene derivative, $N_4P_4(NHPr^i)_2(NMe_2)_6$ (ref. 7) and its hydrochloride adduct. The precise reasons for these differences are by no means obvious but there is little doubt that electronic and steric factors affecting both nucleophile and substituent must be taken into consideration.

Phosphorus-31 NMR spectroscopy is a useful aid in the characterisation and estimation of bicyclic phosphazenes as the latter are invariably difficult to separate from the octakis(amino)cyclotetraphosphazenes that are always formed in these reactions with an excess of primary amine. The chemical shifts of phosphorus nuclei of bicyclic phosphazenes occur downfield (by 10-12 ppm) from those associated with fully aminolysed derivatives of $N_4P_4Cl_8$ (ref. 6,8). The bicyclic phosphazenes, $N_4P_4(NHR)_6(NR)$ (R = Me, Et, Pr^n, Bu^n) give rise to symmetrical A_2B_2 patterns and are readily analysed[9] (Table 2). The phosphorus-31 NMR spectrum of the isopropylamino bicyclic derivative contains three strong lines and several weak, outer lines centred at δ12.0. This observation indicates that the chemical shifts of antipodal phosphorus nuclei P(2) (6) and P(4) (8) (see structures I and II) are almost identical. A similar spectrum was reported recently for the unique, bicyclic phosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$, containing only secondary amino substituents[10].

Phosphorus-31 NMR data for the asymmetric, bicyclic phosphazenes[6], $N_4P_4(NMe_2)_5(NHR')(NR)$, are also given in Table 2. The spectra of these derivatives are of the A_2BC type and iterative computation is essential for their analysis. The experimental and simulated spectra of

Table 2—Phosphorus-31 $\{^1H\}$NMR Data for Bicyclic Phosphazenes[a]

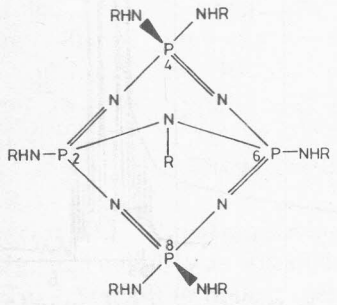
Phosphazene	δP(4),P(8)		δP(2)		δP(6)	$^2J(P-N-P)$(Hz)		
$N_4P_4(NHMe)_6(NMe)$[b]	21.5		—	18.5	—	39.0		
$N_4P_4(NHEt)_6(NEt)$[c]	18.6		—	15.3	—	40.9		
$N_4P_4(NHPr^n)_6(NPr^n)$	18.5		—	15.5	—	41.2		
$N_4P_4(NHBu^n)_6(NBu^n)$	18.7		—	15.5	—	41.4		
$N_4P_4(NHPr^i)_6(NPr^i)$	—	12.0[d]	—			—		
$N_4P_4(NMe_2)_5(NHMe)(NMe)$[e]	21.7		20.7		20.6	44.0[f],	43.9[g],	32.5[h]
$N_4P_4(NMe_2)_5(NHEt)(NEt)$[i]	22.5		19.7		18.9	42.7[f],	42.7[g],	33.0[h]
$N_4P_4(NMe_2)_5(NHPr^n)(NPr^n)$[j]	22.4		—	19.5	—	43.4		
$N_4P_4(NMe_2)_5(NHBu^n)(NBu^n)$	22.4		—	19.6	—	43.3		
$N_4P_4(NMe_2)_5(NHBu^t)(NEt)$	20.6		19.6		16.1	46.5[f],	41.2[g],	34.6[h]
$N_4P_4(NMe_2)_5(NHCH_2Ph)(NCH_2Ph)$[i]	22.0		19.3		18.9	47.1[f],	40.7[g],	23.4[h]

(a) See structures (I) and (II) for numbering of phosphorus atoms. (b) Data from reference 4.
(c) Data from reference 5. (d) Approximate centre of symmetrical pattern of lines.
(e) Assignment of δP(2)P(6) tentative, (f) ^2J [*P*(2)-*P*(4)]. (g) ^2J[*P*(4)-*P*(6)]
(h) ^2J [*P*(2)-*P*(6)], *i* Assignment of δ*P*(2),*P*(6) based on reference 7
(j) Data from reference 6.

$N_4P_4(NMe_2)_5(NHBu^t)(NEt)$ are shown in Fig. 1. The observation that a *t*-butylamino substituent on phosphorus results in a significant upfield shift[6] permits a confident assignment of the P(6)-$NHBu^t$ phosphorus (δ16.1). The effect of the *t*-butylamino substituent can also be observed in the ^{31}P NMR spectrum of the related cyclotetraphosphazene derivative[6], 2-*trans*-6-N_4P_4 $(NHBu^t)$-(NHEt) $(NMe_2)_6$. The spectrum has been analysed with the aid of computer simulation and the shift at highfield (δ2.0) is assigned to the $\equiv P(NMe_2)(NHBu^t)$ phosphorus nucleus. The other parameters are $\delta P(NMe_2)_2 = 8.3$, $\delta P(NMe_2)$ (NHEt) = 5.9; $^2J[P(NMe_2)_2 - P(NMe_2)(NHBu^t)] = 39.0$ Hz, $^2J[P(NMe_2)_2 - P(NMe_2)(NHEt)] = 41.0$ Hz, $^4J[P(NMe_2)(NHBu^t) - P(NMe_2)(NHEt)] = -1.0$ Hz.

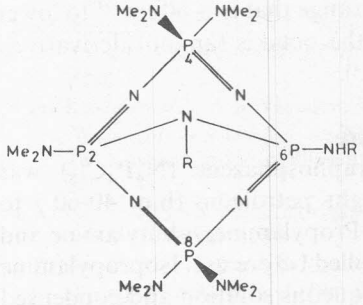
The ^1H NMR spectrum of mixtures of bicyclic phosphazene, $N_4P_4(NHR)_6NR$ (R = *n*-Pr, *i*-Pr, *n*-Bu), and octakis (amino) derivative are complex because of overlapping signals and it has only been possible to determine some of the parameters for the *n*-propylamino derivative, $N_4P_4(NHPr^n)_6(NPr^n)$. These proton chemical shifts and their assignments (based on guidelines established previously[4,6]) are given in structure (III)

The infrared spectra of bicyclic phosphazenes have distinctive bands that are absent in the spectra of fully aminolysed cyclotetraphosphazenes. A characteristic feature is the presence of bands in the 800-860 cm^{-1} region[4] which arise from the bridging P-N-P unit—the phosphazane part of the bicyclic skeleton[11]. In addition, the ring-stretching vibration [$\nu P=N$] for



I

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



II

R = R′ = Me, Et, Pr^n, Bu^n, CH_2Ph

R = Et ; R′ = Bu^t

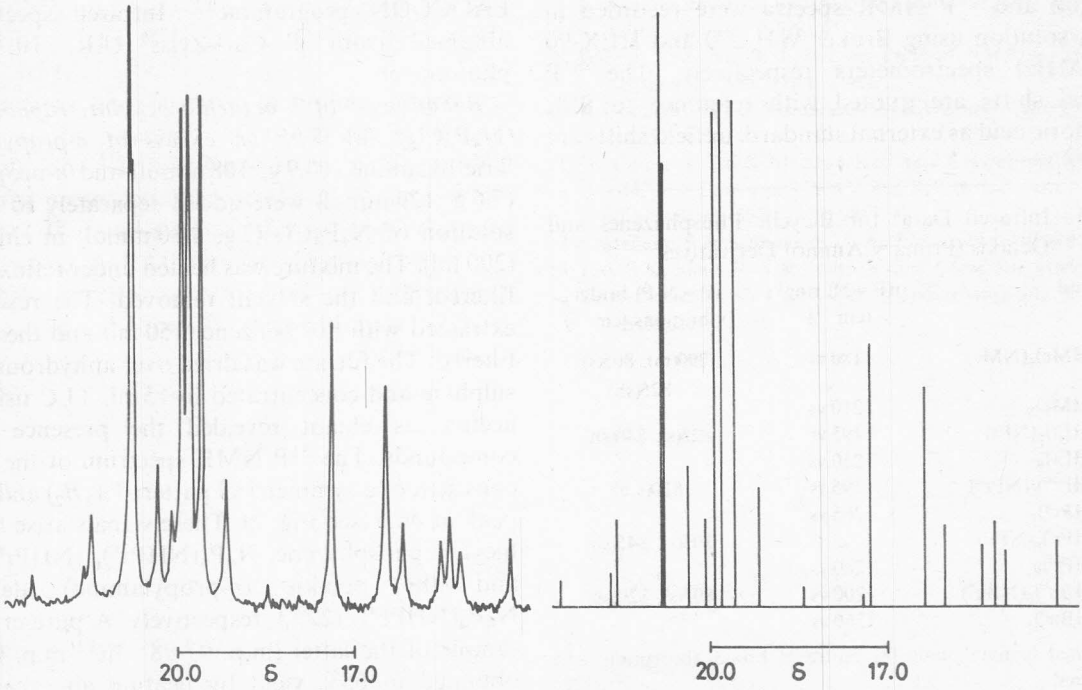
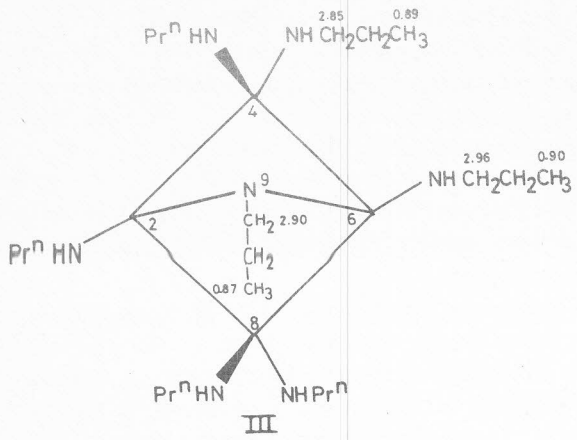


Fig. 1—Phosphorus-31 {^1H}-NMR spectrum of $N_4P_4(NMe_2)_5(NHBu^t)(NEt)$: experimental and simulated



III

(Corners of the square in III represent P atoms; nitrogen atoms linking the phosphorus atoms are omitted)

alkylamino-substituted, bicyclic phosphazenes occurs at 1170-1195 cm^{-1}, a range that is $\sim 60\,cm^{-1}$ to lower energy than that of the octakis (amino) derivatives, $N_4P_4(NHR)_8$ (Table 3).

Experimental Procedure

Octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) was recrystallised from light petroleum (b.p. 40-60°) to constant m.p. 124°. *n*-Propylamine, *n*-butylamine and benzylamine were distilled before use. Isopropylamine was generated from aqueous solution and condensed at −70°C after drying with potassium hydroxide. Triethylamine was distilled over sodium chips. Organic solvents were purified by conventional methods.

Proton and ^{31}P NMR spectra were recorded in $CDCl_3$ solution using Bruker WH-270 and HEX-90 (36.43 MHz) spectrometers respectively. The ^{31}P chemical shifts are quoted with reference to 85% phosphoric acid as external standard; upfield shifts are negative. Computer analyses of the NMR spectra were carried out using a modified version of the LAOCOON programme[12]. Infrared spectra were obtained from a Carl-Zeiss U.R. 10 spectrophotometer.

Table 3—Infrared Data[a] for Bicyclic Phosphazenes and Octakis (Primary Amino) Derivatives

Compound	ν(P=N) ring[b] (cm^{-1})	(P−N-P) bridge vibrations (cm^{-1})
$N_4P_4(NHMe)_6(NMe)$	1180 vs	790(m), 805(s), 825(sh)
$N_4P_4(NHMe)_8$	1210 vs	
$N_4P_4(NHEt)_6(NEt)$	1195 vs	825(s), 840(sh)
$N_4P_4(NHEt)_8$	1250 vs	
$N_4P_4(NHPr^n)_6(NPr^n)$	1195 vs	820(s,b)
$N_4P_4(NHPr^n)_8$	1265 vs	
$N_4P_4(NHPr^i)_6(NPr^i)$	c	805(s), 845(sh)
$N_4P_4(NHPr^i)_8$	1280 vs	
$N_4P_4(NHBu^n)_6(NBu^n)$	1200 vs	805(s), 820(sh)
$N_4P_4(NHBu^n)_8$	1260 vs	

(a) Obtained in nujol mull; (b) centre of broad absorption; and (c) obscured.

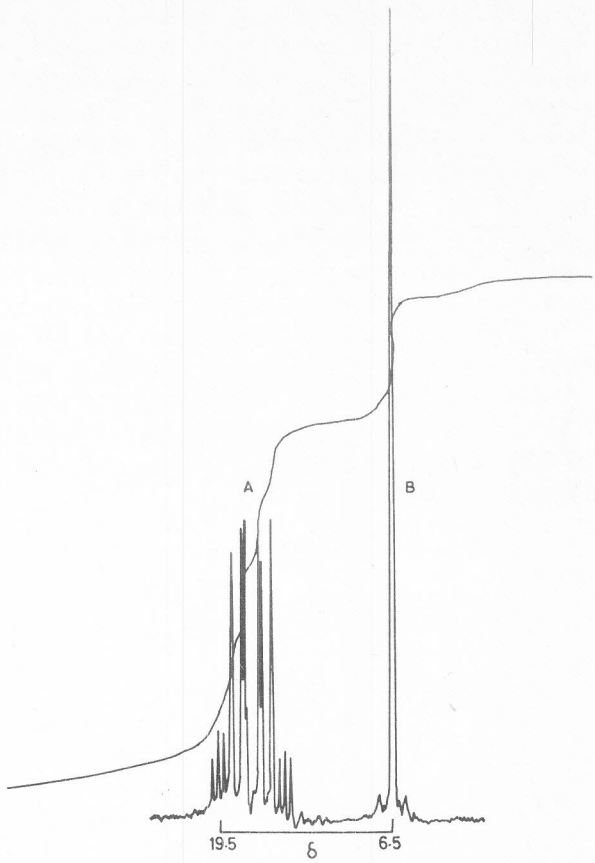


Fig. 2—Phosphorus-31 $\{^1H\}$-NMR spectrum of a mixture of (A) $N_4P_4(NHPr^n)_6(NPr^n)$ and (B) $N_4P_4(NHPr^n)_8$

Reactions of octachlorocyclotetraphosphazene ($N_4P_4Cl_8$): (a) *With an excess of n-propylamine*—Triethylamine (10.9 g, 108 mmol) and *n*-propylamine (7.6 g, 129 mmol) were added separately to a stirred solution of $N_4P_4Cl_8$ (2 g, 4.30 mmol) in chloroform (200 ml). The mixture was heated under reflux for 8 hr, filtered, and the solvent removed. The residue was extracted with hot benzene (150 ml) and the solution filtered. The filtrate was dried over anhydrous sodium sulphate and concentrated to 15 ml. TLC using ethyl acetate as eluant revealed the presence of two compounds. The ^{31}P NMR spectrum of the mixture consisted of a symmetrical pattern (A_2B_2) and a single peak at δ6.5 (see Fig. 2). These signals arise from the bicyclic phosphazene, $N_4P_4(NHPr^n)_6$ ($NHPr^n$) (60%), and the octakis (*n*-propylamino) derivative, $N_4P_4(NHPr^n)_8$ (22%), respectively. A pure crystalline sample of the latter (m.p. 97-98°, lit[13] m.p. 98°) was obtained in 65% yield by heating an excess of *n*-propylamine and $N_4P_4Cl_8$ in diethyl ether for 10 hr.

The ^{1}H NMR data for $N_4P_4(NHPr^n)_8$ are: δ0.92(CH_3), 1.52(CH_2, β), 2.83 (CH_2, α), 3.0 (NH).

(b) *With an excess of n-butylamine*—*n*-Butylamine (9.4 g, 129 mmol) was allowed to react with the $N_4P_4Cl_8$ (2g, 4.3 mmol) in chloroform (200 ml) and triethylamine (10.9 g, 108 mmol) as described in experiment (a). TLC showed the presence of two compounds with similar R_f values but it was not possible to crystallise either of them. The ^{31}P NMR spectrum of the mixture consisted of an intense singlet (δ6.9) for the octa(amino) derivative, $N_4P_4(NHBu^n)_8$ (60%) and a symmetrical group of signals at low field arising from the bicyclic phosphazene, $N_4P_4(NHBu^n)_6(NBu^n)$ (16%). A pure sample of the octakis (*n*-butylamino) compounds was prepared by the reaction of *n*-butylamine (14.1 g, 193 mmol) with $N_4P_4Cl_8$ (1.0 g, 2.15 mmol) in methyl cyanide (200 ml). The mixture was heated under reflux for 48 hr, filtered and the solvent evaporated. The residue was extracted with light petroleum (40 ml), *n*-butylamine hydrochloride filtered off and the filtrate was concentrated to 10 ml to give crystals of $N_4P_4(NHBu^n)_8$, m.p. 81-83° (lit[13] m.p. 81°) (1.1 g, 68.3%); ^{1}H NMR : 0.90(CH_3), 1.35 (CH_2, γ), 1.45(CH_2, β), 2.80 (CH_2, α); $^{31}P\{^1H\}$: 6.9(*s*).

(c) *With an excess of isopropylamine*—Isopropylamine (19.0 g, 323 mmol) was allowed to react with $N_4P_4Cl_8$ (2 g, 4.3 mmol) in boiling methyl cyanide (200 ml) for 8 hr. The solvent was evaporated and the residue extracted with light petroleum (40 ml). The extract was concentrated to 10 ml to obtain octakis (isopropylamino)cyclotetraphosphazene, $N_4P_4(NHPr^i)_8$, m.p. 123-25°C (1.9 g, 67.6%); MS 644; ^{1}H NMR : 1.17 (CH_3), 2.2 (NH), 3.35 (CH); $^{31}P\{^1H\}$: 1.1 (*s*).

The reaction was repeated in boiling chloroform (200 ml) in the presence of triethylamine (10.9 g, 108 mmol). The ^{31}P NMR spectrum of the product showed the presence of the octakis (isopropylamino) derivative (70%) and a minor component (11%) with signals centred at δ12.0 ppm (see Discussion).

(d) *With an excess of benzylamine*—A mixture of $N_4P_4Cl_8$ (2g, 4.3 mmol), triethylamine (32.7 g, 324 mmol) and benzylamine (41.4 g, 387 mmol) in chloroform (200 ml) was heated under reflux for 72 hr. The ^{31}P NMR spectrum of the oily product showed only a singlet at δ4.8; an authentic sample[14] of the octakis (benzylamino) compound, $N_4P_4(NHCH_2Ph)_8$, gave a singlet at δ4.3.

Acknowledgement

We are indebted to the UGC, New Delhi and to the Overseas Development Administration (UK) for support. Our thanks are also due to Kings' College, University of London for phosphorus-31 NMR spectra.

References

1 Krishnamurthy S S, Sau A C, Vasudeva Murthy A R, Keat R, Shaw R A & Woods M, *J Chem Soc Dalton Trans*, (1976) 1405.

2 Krishnamurthy S S, Sau A C, Vasudeva Murthy A R, Keat R, Shaw R A & Woods M, *J Chem Soc, Dalton Trans*, (1977) 1980.

3 (a) Krishnamurthy S S, Vasudeva Murthy A R, Shaw R A & Woods M, *J Indian Inst Sci*, **61B** (1979) 57.
(b) Krishnamurthy S S, Shaw R A & Woods M, *Curr Sci*, **45** (1976) 433.

4 Krishnamurthy S S, Ramachandran K & Woods M, *J chem Res*, (1979) (S) 92; (M) 1259.

5 Krishnamurthy S S, Sau A C, Vasudeva Murthy A R, Shaw R A, Woods M & Keat R, *J chem Res*, (1977) (S) 70; (M) 860.

6 Krishnamurthy S S, Ramachandran K, Sau A C, Shaw R A, Vasudeva Murthy A R & Woods M, *Inorg Chem*, **18** (1979) 2010.

7 Krishnamurthy S S, Ramachandran K & Woods M, *Phosphorus Sulfur*, **9** (1981) 323.

8 Krishnamurthy S S, Sau A C & Woods M, *Adv Inorg Chem Radiochem*, **21** (1978) 41.

9 Wiberg K & Nist B J, *Interpretation of NMR spectra*, (W A Benjamin, New York, 1962.

10 Krishnamurthy S S, Sundaram P M & Woods M, *Inorg Chem*, **21** (1982) 406.

11 (a) Cameron T S & Mannan Kh, *Acta Crystallogr*, **33B** (1977) 443; (b) Cameron T S, Cordes R E & Jackman F A, *Acta Crystallogr*, **35B** (1979) 985.

12 Castellano S & Bothner-by A A, *J chem Phys*, **41** (1964) 3863.

13 Ray S K, Shaw R A & Smith B C, *J Chem Soc*, (1963) 3236.

14 Ramachandran K, Ph D Thesis, Indian Institute of Science, Bangalore, 1978.