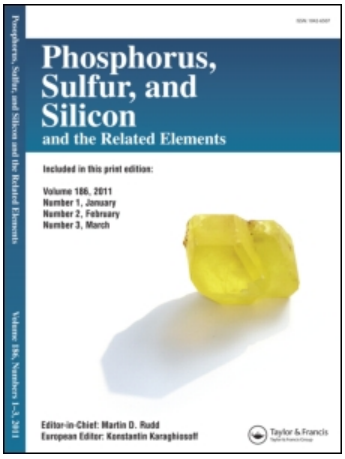

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STUDIES OF PHOSPHAZENES. PART VI.[1] THE PREPARATION OF THE ISOMERIC TETRACHLOROBIS-ISOPROPYLAMINOCYCLOTRIPHOSPHAZATRIENES

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STUDIES OF PHOSPHAZENES. PART VI.[1] THE PREPARATION OF THE ISOMERIC TETRACHLOROBIS-ISOPROPYLAMINOCYCLOTRIPHOSPHAZATRIENES

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The three isomers of $N_3P_3Cl_4(NHPr^i)_2$ have been prepared and separated by gas–liquid chromatography. Their structures have been assigned on the basis of ^1H and ^{31}P nmr data.

INTRODUCTION

The reaction of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with isopropylamine was reported by Das *et al.* and the isopropylamino-derivatives, $N_3P_3Cl_{6-n}(NHPr^i)_n$ (n = 1, 2, 4, 6) were isolated.[2] In an attempt to prepare the bis-derivative in large quantities, we repeated the reaction of $N_3P_3Cl_6$ with four mole equivalents of isopropylamine in various organic solvents but failed to reproduce the earlier results. Our work has led to the isolation of all the isomeric bis-isopropylamino derivatives, $N_3P_3Cl_4(NHPr^i)_2$. We describe in this paper the preparative details and nmr spectroscopic data.

EXPERIMENTAL

Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (I), was recrystallized from light petroleum (bp 60–80°C). Isopropylamine and organic solvents were purified by conventional methods. Gas–liquid chromatography experiments were carried out with a Varian Aerograph Series 1800. A steel column 20 ft × ⅜ in packed with either 5% OV-17 or 2½% SE-30 on 60/80N AW-DMCS was used. ^1H and ^{31}P nmr spectra were recorded with Jeol MH 100 and Bruker HFX-90 spectrometers respectively.

General Procedure

Isopropylamine (4.72 g, 0.8 mol) was added dropwise to a stirred solution of $N_3P_3Cl_6$ (I) (6.96 g, 0.2 mol) in the organic solvent (100 cm³) at 25°C in the absence of atmospheric moisture. The reaction mixture was heated under reflux for 3 hr, cooled and filtered to remove isopropylamine hydrochloride. Evaporation of the filtrate gave an oily residue. Thin layer chromatography (silica gel; benzene eluant) showed the presence of two components in this residue; the faster moving component corresponded to the mono-derivative, $N_3P_3Cl_5(NHPr^i)$ (II), isolated and characterized previously.[2] Numerous attempts to crystallize the oily residue were unsuccessful. The oil was chromatographed on silica gel to give the mono-compound (II) mp 55–56° and another oily substance (single spot on tlc; mass spectrum: parent ion at m/e = 391 corresponds to $N_3P_3Cl_4(NHPr^i)_2$). Attempts to crystallize the latter were also unsuccessful. Examination of this oil by glc showed the presence of three components. Small quantities (50 mg) of each component were separated by preparative scale glc. The variation of the relative yield of these products in different solvents was determined from glc traces. The results are summarized in Table I.

RESULTS AND DISCUSSION

The ^1H and ^{31}P nmr data for the three bisisopropylamino-derivatives (III–V) are shown in Table II. Data for $N_3P_3Cl_{6-n}(NHPr^i)_n$ [n = 1, 4(gem), 6] are also included for comparison. The bis-isomer (III) which has the lowest glc retention time clearly possesses a geminal structure. Its ^{31}P nmr spectrum (Figure 1a) consists of a doublet and a triplet with relative intensities 2:1. ^1H Decoupling experiments show that the triplet arises from the $\equiv P(NHPr^i)_2$

TABLE I
Gas–Liquid Chromatography Data

No.	Compound	mp °C	Glc retention time (min.)		Relative yields of products[c] (%)			
			OV17[a]	SE30[b]	Et_2O	$CHCl_3$	PhH	MeCN
(II)	$N_3P_3Cl_5(NHPr^i)$	55–56[d]	23	14	56	55	4	3
(III)	gem-$N_3P_3Cl_4(NHPr^i)_2$	114	32	22	4	10	10	25
(IV)	*trans*-$N_3P_3Cl_4(NHPr^i)_2$[e]	76–78	41	31	36	28	61	37
(V)	*cis*-$N_3P_3Cl_4(NHPr^i)_2$[f]	98–99	46	37	4	5	25	35

[a] Operating temperature 250°C, carrier gas pressure 12 psi.
[b] Operating temperature 225°C, carrier gas pressure 10 psi.
[c] For conditions, see experimental.
[d] Lit[2] mp 54–55°.
[e] Found: C, 18.5; H, 3.9; $C_6H_{16}Cl_4N_5P_3$ requires C, 18.3; H, 4.1.
[f] Found: C, 18.2; H, 4.0.

TABLE II
Nuclear Magnetic Resonance

No.	Compound	δ^1H[a]			$\delta^{31}P$[b]			$^2J(P–P)$ (Hz)
		NH	CH	CH_3	PCl_2	PClR	PR_2	
(II)	$N_3P_3Cl_5(NHPr^i)$	3.2	3.5_5	1.23	20.4	17.0		46.5
(III)	gem-$N_3P_3Cl_4(NHPr^i)_2$	2.3	3.4_0	1.17	19.8		6.2	45.5
(IV)	*trans*-$N_3P_3Cl_4(NHPr^i)_2$	3.1	3.5_5	1.23	21.3	19.1		48.8
(V)	*cis*-$N_3P_3Cl_4(NHPr^i)_2$	3.2	3.5_5	1.22	21.9	19.0		48.8
(VI)	gem-$N_3P_3Cl_2(NHPr^i)_4$	2.1	3.3_5	1.12	22.2[c]		9.4[c]	49.4[c]
(VII)	$N_3P_3(NHPr^i)_6$	1.9	3.3_5	1.08			12.6[c]	

[a] $CDCl_3$ solution.
[b] 36.43 MHz; CD_2Cl_2 solution; reference 85% aqueous H_3PO_4 (external); upfield shifts are negative.
[c] Data from Ref. 8.

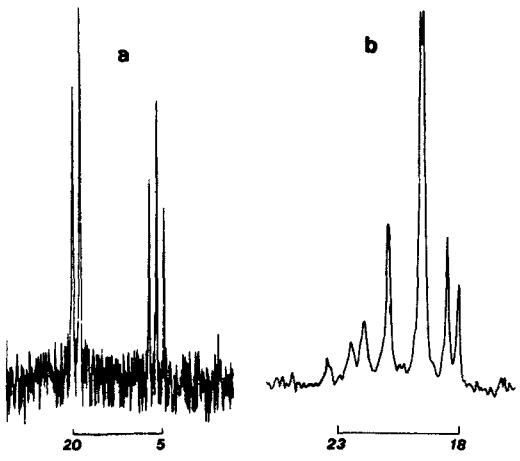

FIGURE 1 $^{31}P\{^1H\}$nmr spectrum of (a) geminal-$N_3P_3Cl_4(NHPr^i)_2$ and (b) *cis*-$N_3P_3Cl_4(NHPr^i)_2$.

group. Compounds (IV) and (V) have nongeminal structures. Their ^{31}P nmr spectra are of the AB_2 type (see Figure 1b). The above structural assignments are supported by the observed chemical shifts of the N–H protons. [δ_{NH}(gem)1.9–2.3; δ_{NH}(nongem)3.2; see also Refs. 3, 4.]

The glc retention times of pairs of nongeminal bis-aminotetrachlorocyclotriphosphazatrienes, $N_3P_3R_2Cl_4$ (R = NMe_2,[5] NEt_2,[6] NMePh[7]) have been reported. The retention of the *cis*-isomer is greater than that of the *trans*-isomer. Hence compounds (IV) and (V) have been assigned *trans*- and *cis*-structures respectively.

The chemical shifts of CH and CH_3 protons for compounds (III–V) are in the order of $\delta_{(gem)} < \delta_{(nongem\text{-}cis)} \leqslant \delta_{(nongem\text{-}trans)}$. A similar trend is observed for many aminochlorocyclophosphazene derivatives. Another interesting trend is the regular

increase of $\delta_{P(NHPr^i)_2}$ for the geminal derivatives, (III), (VI) and (VII). The $\equiv PCl(NHPr^i)$ signals are shifted upfield relative to the $\equiv PCl_2$ signals as noted previously for primary amino derivatives.[8]

Table I shows the relative yields of chloro-isopropylamino derivatives (II–V) in boiling organic solvents. Reactions in diethyl ether or chloroform do not go to completion (3 h) and the mono-derivative, $N_3P_3Cl_5(NHPr^i)$ (II) is the main product. Benzene and methyl cyanide are the preferred solvents for the preparation of the bis-isomers (III–V). The formation of the nongeminal isomers (IV, V) presumably involves an $S_N2(P)$ mechanism. An interesting feature is the much larger amount of the *cis*-isomer (V) formed in methyl cyanide compared to that in benzene. Other studies have also shown that enhanced yields of *cis*-isomers are obtained in methyl cyanide when the hexachloride (I) reacts with *secondary* amines.[6b,9] This enhanced yield of the *cis*-isomer may be due to a secondary isomerization step of the type discussed previously.[10] Goldschmidt and Segev have demonstrated that either *cis*- or *trans*-$N_3P_3Cl_4(NMe_2)_2$ rapidly equilibrate in methyl cyanide in the presence of dimethylamine hydrochloride: the mixture of isomers obtained contains a slight excess of the *trans*-compound.[11]

A further point of interest is the higher proportion of the geminal bis-isomer (III) [compared to the nongeminal isomers (IV, V)] obtained in chloroform and methyl cyanide. The formation of the geminal compound can be rationalized by assuming a proton abstraction mechanism.[12] Also, nuclear quadrupole resonance studies indicate that the P–Cl bond of the $\equiv PCl(NHPr^i)$ group of the mono-derivative (II) is the most ionic in character.[13] It seems likely that methyl cyanide, a solvent of high dielectric constant, will facilitate the ionization of this $\equiv$P–Cl bond. On the other hand, chloroform may provide a good medium for solvation of the departing chloride ion.

Finally, it should be stressed that studies of the effect of solvents on the chlorine replacement pattern of chlorocyclophosphazenes are still very much in their infancy.[6b,14–16] Very few conclusions can be drawn with certainty at the moment and further hypotheses must await the availability of many more experimental findings.

Reactions of $N_3P_3Cl_6$ with other primary amines have been reported. Reactive amines ($MeNH_2$,[17] $EtNH_2$[3]) give rise to nongeminal bis-derivatives, $N_3P_3Cl_4(NHR)_2$, with the *trans*-isomer predominating.† Only bis-compounds with geminal structures have been obtained from reactions with less reactive amines (*t*-butylamine[12] and aniline[19]). Hence, an amine of intermediate reactivity should give both geminal and nongeminal bis-derivatives as is indeed observed for isopropylamine in this investigation. Geminal and nongeminal bis-derivatives were also obtained in the reaction of $N_3P_3Cl_6$ with benzylamine.[4]

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† A small quantity of gem-$N_3P_3Cl_4(NHMe)_2$ was also obtained. Higher yields are formed in the presence of a tertiary base.[18]

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