REACTION OF HEXACHLOROCYCLOTRIPHOSPHAZENE WITH 2,4,6-TRIMETHYLANILINE

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ABSTRACT

Hexachlorocyclotriphosphazene reacts with 2,4,6-trimethylaniline to give only mono- and di-substituted derivatives. The ditrimethyl-anilinotetrachloro-cyclotriphosphazene was characterised by its ^{31}P nmr spectrum as the geminal isomer and its crystal data are presented. Crystals of the geminal isomer are monoclinic, a = 12,393(16), b = 17.608(23), c = 14.717(19), Å, β = 114.88(7)°, Z = 4, space group P21/C.

INTRODUCTION

REACTIONS of chlorocyclophosphazenes with various amines have been studied extensively; both geminal and non-geminal substitution patterns depending on the nature of the amines used being observed[1,2]. We have investigated the title reaction with a view to prepare the fully substituted phosphazene and to explore its ligating properties towards metal ions.

EXPERIMENTAL

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, prepared earlier[3], was purified by repeated recrystallisation from petroleum ether (m.p. 113° C, literature value 112.8° C). 2,4,6-Trimethylaniline (TMA) and triethylamine were distilled from KOH pellets prior to use. Benzene was distilled from P_2O_5. ^1H and ^{31}P nmr spectra were obtained on a Varian XL-100 FT instrument. Infrared spectra (as mulls in nujol or hexachlorobutadiene, or as a thin film) were recorded on a Perkin-Elmer 577 grating infrared spectrophotometer. Mass spectra were obtained on a VG Micromass 70–70F instrument.

Reaction of $N_3P_3Cl_6$ with 2,4,6-trimethylaniline

A solution of trimethylaniline (7.6 g, 56.3 mmol) and triethylamine (5.3 g, 52.5 mmol) in 50 ml benzene was added dropwise with vigorous stirring to a refluxing solution of $N_3P_3Cl_6$ (3 g, 8.6 mmol) in 50 ml benzene under nitrogen and the reaction was continued for 10 days. The solution was then treated with water and the solvent distilled from the organic phase after drying it over anhydrous Na_2SO_4. A pasty dark yellow material, whose mass spectrum showed the presence of only mono- and di-substituted derivatives was obtained. The above reaction was repeated using the phosphazene (10 g) and the trimethylaniline in 1 : 1.2 molar ratio. The crude product, which contained less of polymeric material (as evident from the formation of a resinous compound as before), showed the presence of mono- and di-substituted derivatives (mass spectrum). Thin layer chromatography showed the presence of one major and two minor components. The resinous material could not be characterised. The crude product when treated with a mixture of petroleum ether (5 parts) and $CHCl_3$ (1 part) yielded an insoluble compound (free from resinous materials) which on fractional recrystallisation from CH_2Cl_2 gave 1.5 g of the di-substituted compound, m.p. 219–220° C. Anal. Calcd. for: $N_5P_3Cl_4C_{18}H_{24}$ C, 39.66; H, 4.44; N, 12.85; Cl, 26.01; Found: C, 40.02; H, 4.64; N, 13.43; Cl, 26.52. Thin layer chromatography showed it to be a single compound.

RESULTS AND DISCUSSION

The rate of nucleophilic displacement of a chloride ion from a chlorophosphazene is usually increased by an electron withdrawing group such as fluorine[4] and decreased by an electron releasing group such as amino group[5]. The fact that heavily substituted derivatives are not formed in the present reaction indicates that substitution rate is highly retarded which can be attributed to both electronic and steric factors. From thin layer chromatographic evidence it appears that the substitution follows predominantly a geminal pathway. The mass spectrum of the compound shows besides an intense parent ion peak (543-551) with the associated isotopic pattern for $N_5P_3Cl_4C_{18}H_{24}N_2$, fragment peaks corresponding to the loss of a methyl group, trimethylanilino group and chloro-trimethylanilino group. In the ^1H nmr spectrum the ortho-methyl protons which are more shielded in

TABLE 1

Nuclear magnetic resonance parameters[a]

	$C_6H_2(CH_3)_3NH_2$	$N_3P_3Cl_4[HNC_6H_2(CH_3)_3]_2$	$N_3P_3Cl_6$
NH	3.51	4.19[b]	—
meta–H	6.79	6.88	—
para–CH_3	2.23	2.25	—
ortho–CH_3	2.19	2.39	—
PCl_2	—	20.00[c]	19.30
$P(TMA)_2$	—	3.21[d]	—
$J_{PNP/Hz}$	—	40	—

[a]All in $CDCl_3$; shifts in ppm. relative to internal tetramethylsilane (^1H) or external 80% H_3PO_4(^{31}P). Positive shifts to low field of resonance. [b]$J_{H\text{-}N\text{-}P} \doteq 11$ Hz. [c]doublet. [d]triplet.

TMA are observed to be more deshielded in the present compound as expected. The NH proton is significantly deshielded in the compound as expected. The coupling of the NH proton with phosphorous, which is normally unresolved in similar known compounds, is observed in the present compound. The ^{31}P nmr spectrum, which is interpretable in terms of an AB_2^2 spin system, not only differentiates mono- from di-substitution but also shows that the substitution is indeed geminal *i.e.* the two trimethylanilino groups in the compound are bonded to the same phosphorus atom. The δ_P values are consistent with the presence of a PCl_2 and $P(—TMA)_2$ groups[6]. The high field triplet also shows signs of splitting due to the coupling of ^{31}P with NH protons, thereby substantiating the geminal mode of substitution. The ^1H and ^{31}P nmr parameters are given in table 1.

Although unambiguous assignments of bands in the infrared spectrum of the compound could not be made, some salient features could be recognised. The symmetry in the parent phosphazene ($N_3P_3Cl_6$), which is very nearly D_{3h} is reduced in the compound due to substitution of chlorine by trimethylanilino groups. Consequently the degenerate band for ϑ_{as}(PNP) vibration (E') at 1210 cm^{-1} in the parent phosphazene[7] is split, the new bands appearing at 1210 cm^{-1} and 1180 cm^{-1} respectively. The NH_2 stretching vibrations in TMA appear respectively at 3460 cm^{-1} and 3380 cm^{-1}. The ϑ_{NH} (3340 cm^{-1}) in the compound is reduced as expected. By analogy with dimethyl-aminochlorotriphosphazenes[8,9] the bands of medium intensity at 740 cm^{-1} and 725 cm^{-1} are respectivley assigned to $\vartheta_{as}PN_2$ and ϑ_sPN_2. The ring elongation mode (E'), which is degenerated in the parent phosphazene, is split in the compound to give new intense bands at 970 and 945 cm^{-1}. The bands at 605, 600 and 575 cm^{-1} are assigned to ϑPCl_2 vibrations.

The greatest interest in the structures of inhomogenously substituted phosphazenes is in the inequality of ring bond lengths induced by the substituents. The bond length inequalities observed in gem-dimethylhexafluorocyclotetraphosphazene are interpreted in terms of perturbation theory applied to a delocalised π-electron system[10]. In order to get more structrual information on geminally di-substituted phosphazene derivatives we have taken up the crystal structure determination of the present compound. The oscillation and Weissenberg X-ray photographs with Cu-K_α radiation show that the crystal system is monoclinic with sytematic absences of $h\,o\,l$ (l odd) and $o\,k\,o$ (k odd). The space group is, therefore, P21/C. The unit cell parameters have been refined using the powder diffraction data.

Crystal data are:

$N_5P_3Cl_4C_{18}H_{24}$ f_w: 545.16
monoclinic, $a = 12.393(16)$, $b = 17.608(23)$, $c = 14.717(19)$, Å $\beta = 114.88(7)°$, D_m 1.22 g cm^{-3} (flotation), $D_c \doteq 1.24$ g.cm^{-3}, $Z = 4$, space group P21/C, $V = 2914$ Å^3, $\lambda = 1.5418$ Å.

Powder diffraction data:

	d_{obs}(Å)	d_{calc}(Å)	h	k	l	I/I_o
1	8.934	8.934	1	1	0	21
2	7.284	7.287	$\bar{1}$	1	2	100
3	6.707	6.684	0	2	1	16
4	6.109	6.157	1	2	0	3
5	5.609	5.621	2	0	0	5
6	5.505	5.508	1	0	2	7
		5.488	$\bar{2}$	1	2	
7	5.246	5.251	2	1	0	14
8	4.623	4.610	$\bar{2}$	2	2	5
9	4.332	4.314	0	2	3	7

	d_{obs}(Å)	d_{calc}(Å)	h	k	l	I/I_o
10	4.152	4.150	1	3	1	2
		4.178	$\bar{2}$	2	3	
11	4.040	4.033	$\bar{2}$	1	4	8
12	3.917	3.902	$\bar{3}$	1	1	10
13	3.754	3.765	2	1	2	
		3.774	$\bar{1}$	2	4	10
		3.772	$\bar{2}$	3	2	
		3.760	$\bar{1}$	3	3	
14	3.693	3.696	2	3	0	12
		3.672	0	4	0	
15	3.641	3.634	1	2	3	
		3.632	3	1	0	34
		3.645	$\bar{2}$	2	4	
16	3.527	3.528	$\bar{2}$	3	3	
		3.544	$\bar{3}$	2	1	11
		3.514	0	2	4	
17	3.427	3.439	2	2	2	2
18	3.345	3.339	3	2	0	
		3.352	1	0	4	5
		3.338	0	4	2	
19	3.271	3.272	$\bar{1}$	3	4	6
20	3.198	3.187	$\bar{2}$	3	4	8
		3.182	1	3	3	
21	3.048	3.048	2	3	2	
		3.048	3	2	1	2
		3.049	1	2	4	
		3.057	1	4	2	
22	2.979	2.976	3	3	0	
		2.971	2	2	3	3
		2.976	$\bar{2}$	4	3	
23	2.912	2.919	$\bar{3}$	2	5	
		2.900	$\bar{4}$	1	4	3
		2.899	2	4	1	
		2.894	3	1	2	
24	2.862	2.856	1	5	1	3
		2.847	$\bar{4}$	2	2	
25	2.722	2.722	$\bar{3}$	4	1	
		2.711	2	1	4	2
		2.718	4	1	5	
26	2.571	2.574	0	5	3	
		2.567	$\bar{3}$	4	4	3
		2.582	2	2	4	
27	2.249	2.247	$\bar{1}$	5	5	
		2.252	$\bar{5}$	2	5	5
		2.245	$\bar{2}$	5	5	
		2.247	4	2	2	

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CHANGES IN THE TISSUE CONCENTRATION OF GLUTATHIONE AND PROTEIN IN LEAD TOXICITY

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ABSTRACT

The effect of different levels of lead on the reduced glutathione (GSH) and protein concentration of the liver, kidneys and brain was investigated in this study. Lead toxicity increased the GSH concentration of the liver and kidneys but the brain GSH concentration was relatively unaffected. The protein concentration of the organs decreased in lead toxicity. A possible role for GSH in detoxication of lead is indicated.