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Aminolysis Reactions of 1-Dichlorophosphinyl-2,2,2-trichlorophosphazene, $Cl_2P(O)\cdot N{=}PCl_3$

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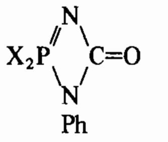
The reactions of 1-dichlorophosphinyl-2,2,2-trichlorophosphazene, $Cl_2P(O)\cdot N{=}PCl_3$*, with methylamine and t-butylamine have been studied. The acyclic amino-derivatives,* $Cl_2P(O)\cdot N{=}PCl_2(NHMe)$*,* $Cl_2P(O)\cdot N{=}PCl_2(NHBu^t)$ *[or its tautomer,* $Cl_2P(O)\cdot NH\cdot PCl_2({=}NBu^t)$*],* $Cl_2P(O)\cdot N{=}PCl(NHMe)_2$*, and* $Cl(Bu^tNH)P(O)\cdot N{=}PCl_2(NHBu^t)$ *have been isolated, the position of chlorine-atom replacement being established by* ^1H *and* ^{31}P *n.m.r. spectroscopy. No evidence for the formation of cyclic phosphazenes,* $\overline{ClRNP(O)\cdot N{=}P}Cl_2$ *(R = Me,* Bu^t*) has been obtained.*

Introduction

Although a wide range of synthetic routes to the cyclophosphazenes have been devised [1, 2], phosphazenes which form part of a four-membered ring remain elusive. Two recent reports [3, 4] of the isolation of such species have proved incorrect [5, 6]. In view of these findings, the claim to have isolated [7] (I) requires further authentication.



(X = Cl, Ph, OPh)

(I)

$Cl_2P(O)\cdot N{=}PCl_3$

(II)

Recent observations [8, 9] that acyclic compounds containing the P–N–P skeleton are readily cyclized by primary amines, and the isolation [10] of phosphazenes which form part of a five-membered ring, led us to investigate the reactions of the phosphazene(II) [11] with primary amines in the hope that, it too, could be induced to undergo a cyclization reaction.

Experimental

Solvents were purified by conventional means. Methylamine was passed through a column of sodium hydroxide pellets and t-butylamine distilled from sodium hydroxide pellets before use. All experiments were carried out under an atmosphere of dry nitrogen. 1-Dichlorophosphinyl-2,2,2-trichlorophosphazene(II), was prepared by a literature method [11]. ^1H n.m.r. spectra were recorded on Jeol C60HL (60 MHz), or Perkin Elmer R 32 (90 MHz) spectrometers and ^{31}P n.m.r. spectra were obtained on the C60HL (24.3 MHz) or in the Pulsed Fourier Transform mode on a Varian XL-100 spectrometer (40.5 MHz).

1-Dichlorophosphinyl-2,2-dichloro-2-methylamino-phosphazene, (III) (R = Me)

Methylamine (1.5 g, 48 mmol) in diethyl ether (30 ml) was slowly added to a stirred solution of 1-Dichlorophosphinyl-2,2,2-trichlorophosphazene(II) (6.4 g, 24 mmol) in diethyl ether (150 ml) at –78 °C. The mixture was allowed to come to ambient temperatures, the methylamine hydrochloride and solvent removed, and the oily residue distilled under reduced pressure to give (III) (R = Me) (0.4 g, 5%) b.p. 145°/0.2 mm, which slowly solidified, m.p. 48–50 °C. *Anal.* Calculated for $CH_4Cl_4N_2OP$: C, 4.5; H, 1.5; N, 10.6; m/e 262 (^{35}Cl only). Found C, 5.0; H, 2.7; N, 10.7%; m/e 261 (P – 1). Distillation resulted in extensive decomposition and low yields; (III) (R = Me) could be obtained in >90% purity (^{31}P n.m.r.) and yields of *ca.* 80% without the distillation step.

1-Dichlorophosphinyl-2-chloro-2,2-bismethylamino-phosphazene, (IV)

This was prepared similarly, although attempted distillation resulted in complete decomposition. An oil was obtained after removal of solvent (83% yield). *Anal.* Calculated for $C_2H_8Cl_3N_3OP_2$: C, 9.3; H, 3.1; N, 16.2; m/e 257 (^{35}Cl only). Found C, 9.0; H, 3.6; N, 16.3%; m/e 257. Although satisfactory analytical data were obtained, the oil was contaminated (*ca.* 10%) with (III) (R = Me) and other unidentified products (^{31}P n.m.r.).

TABLE. ^1H and ^{31}P N.m.r. Data.[a]

Compound	δ_P[b]	$\delta_{P'}$	$^2J(PNP')$[c] (Hz)	δ_{NH}	$^2J(PNH)$[d] (Hz)	δ_{NCH}	$^3J(PNCH)$[d] (Hz)	δ_{NCCH}	$^4J(PNCCH)$[d] (Hz)
$Cl_2P(O){\cdot}N{=}PCl_2(NHMe)$, (III) (R = Me)	+7.0[f]	−9.0[f]	29.9[f]	6.5	±18.6[g]	2.78	±21.0[e]	–	–
$Cl_2P(O){\cdot}N{=}PCl(NHMe)_2$, (IV)	+16.9[f]	−9.8[f]	35.6[f]	5.2	– [f]	2.70	17.0	–	–
$Cl_2P(O){\cdot}N{=}PCl_2(NHBu^t)$[i], (III) (R = Bu^t)	−1.8	−10.8	±25.4	6.0	±14.5[gh]	–	–	1.43	1.5
$(Bu^tNH)ClP(O){\cdot}N{=}PCl_2(NHBu^t)$[i], (V)	−3.9	−6.4	33.2	4.2	7.2[gj]	–	–	1.35	0.6(P′)
				6.1	ca. 11(PNH)			1.45	0.8(P)
$Cl_2P(O){\cdot}N{=}PCl_3$(II)	−0.4	−13.9	17.0	–	–	–	–	–	–

[a] Obtained on $CDCl_3$ solutions at ambient temperatures except where otherwise stated. ^1H n.m.r. data on the methylamino-derivatives was obtained at *ca.* −20 °C. [b] P refers to phosphazenyl-signal, P′ to phosphoryl signal; downfield shifts (p.p.m.) from 85% H_3PO_4 (external) are positive. [c] ±0.5 Hz. [d] ±0.2 Hz. [e] $^3J(HNCH)$ = ±5.3 Hz. [f] C_6D_6 solution. [g] ^1H signal broad at ambient temperatures. [h] $^4J(PNPNH)$ = ±4.9 Hz. [i] or P–NH–P tautomer. [j] $J(P{\cdots}H)$ and $J(P'{\cdots}H)$ observed.

1-Dichlorophosphinyl-2,2-dichloro-2-t-butylaminophosphazene(III) (R = Bu^t) (or its tautomer, see below)

t-Butylamine (4.1 g, 56 mmol) in methylene chloride (20 ml) was slowly added to a solution of 1-dichlorophosphinyl-2,2,2-trichlorophosphazene(II) (7.4 g, 27 mmol) in methylene chloride (90 ml) at −78 °C. The mixture was stirred (2 h) and allowed to come to ambient temperature, the t-butylammonium chloride and solvent removed, leaving a brownish liquid. This crystallised from light petroleum (b.p. 40–60 °C) to give (III) (R = Bu^t) (4.3 g, 72%) m.p. 60–61 °C. *Anal.* Calculated for $C_4H_{10}Cl_4N_2OP_2$: C, 15.7; H, 3.3; N, 9.2; m/e 304 (^{35}Cl only). Found C, 15.4; H, 3.2; N, 9.1%; m/e 289 (P – 15).

1-Chloro(t-butylamino)phosphinyl-2,2-dichloro-2-t-butylaminophosphazene, (V)

This was prepared by a route similar to that employed for (III) (R = Bu^t), using (II) and t-butylamine in a 1:4 molar ratio respectively. A brownish coloured solid (72%) was obtained which resisted attempts at recrystallisation, but gave satisfactory analytical data for (V). *Anal.* Calculated for $C_8H_{20}Cl_3N_3OP_2$: C, 28.05; H, 5.9; N, 12.3; m/e 341 (^{35}Cl only). Found C, 28.3; H, 6.7; N, 12.1%, m/e 326 (P – 15).

Reactions of (III) (R = Me) and of (III) (R = Bu^t) (or its tautomer) with triethylamine were carried out in deuteriobenzene solutions and followed by ^{31}P n.m.r. spectroscopy. The ^{31}P n.m.r. signals of (III) (R = Me) moved upfield and broadened as the concentration of triethylamine was increased to a 1:1 molar ratio. No products were identified. (III) (R = Bu^t) was unaffected by triethylamine and could be recovered almost quantitatively on pumping off solvent and triethylamine.

Results and Discussion

The reaction of (II) with two molar equivalents of methylamine, triethylamine or t-butylamine leads to the formation of mono-amino-derivatives, (III):

$$\underset{\text{(II)}}{Cl_2P(O){\cdot}N{=}PCl_3} + 2NH_2R \longrightarrow \underset{\text{(III) (R = Me, Bu}^t\text{)}}{Cl_2P(O){\cdot}N{=}P(NHR)Cl_2} + NH_3RCl$$

Evidence for the replacement of a phosphazenyl rather than a phosphoryl-chlorine atom comes from a consideration of the ^{31}P chemical shifts in the Table. In (II) the low-field ^{31}P signal has been assigned [12] to the phosphazenyl-phosphorus and this is likely to be the case in the amino-derivatives reported here. Thus in the compounds (III) (R = Me or Bu^t) it is the lower field ^{31}P signal which has

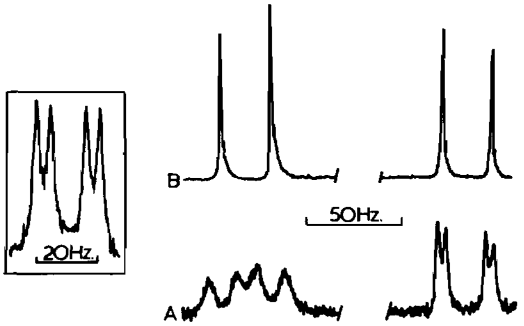


Figure 1. 24.3 MHz ^{31}P n.m.r. spectra of $Cl_2P(O)\cdot N{=}PCl_2$-$NHBu^t$, or its tautomer, $Cl_2P(O)\cdot NH\cdot P({=}NBu^t)Cl_2$, in $CDCl_3$ solution. A, Normal spectrum; B, with ^1H noise decoupling. Inset: ^1H spectrum of the same compound showing N*H* signals only at –25 °C.

multiplet structure because of coupling to N*H*, NC*H*$_3$ or NCC*H*$_3$-protons. The methylamino-substituted ^{31}P signal is at lower field than the t-butylanino ^{31}P signal as found in other P(V) compounds [13]. An unexpected feature of the ^{31}P spectrum of (III) (R = Bu^t) (Figure) was that both ^{31}P nuclei were coupled to the N*H*-proton [$J(P\cdots H) = 14.5$ and 4.9 Hz]. Generally, four bond $P^V N\cdots H$ couplings are not observed, but in exceptional cases may be as large as 2 Hz [14]. The observation of only one such $P\cdots H$ coupling in (III) (R = Me) may indicate that (III) (R = Bu^t) has undergone a tautomerisation step:

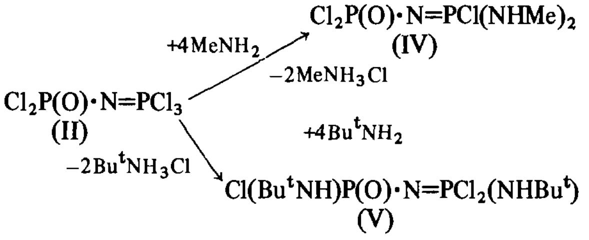
$$Cl_2P(O)\cdot N{=}PCl_2NHBu^t \longrightarrow Cl_2P(O)\cdot NH\cdot PCl_2({=}NBu^t)$$

(III) (R = Bu^t)

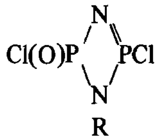
Unfortunately, we have not been able to distinguish between these two forms.

^1H–{^{31}P} and ^{31}P–{^1H} double resonance experiments showed that $^2J(PNP)$, and both $J(P\cdots NH)$ couplings had the same sign (the N*H*-signal was broad at ambient temperatures, but gave a sharp doublet of doublets at –25 °C, the temperature at which the ^1H–{^{31}P} experiments were carried out). Since $^2J(PNH)$ is positive in (III) (R = Me) (see below), it is assumed that $^2J(PNP)$ is positive; this is generally the case for compounds containing the P^V–N–P^V skeleton [15]. Only the low-field ^{31}P signal in (III) (R = Me) showed coupling to the C*H*$_3$ and N*H* protons. The C*H*$_3$ and N*H* signals of the latter compound were broad in the ^1H spectrum at ambient temperatures, but sharpened at –20° to give a doublet of doublets and doublet of quartets respectively. This clearly indicates that a $={PCl_2(NHMe)}$ group is present. ^1H–{^1H} and ^1H–{^{31}P} double resonance experiments showed that $^3J(PNCH)$, $^2J(PNH)$ and $^3J(HNCH)$ all had the same sign, which on the basis of literature data for $^3J(PNCH)$ [16] is positive.

The addition of four molar equivalents of amine to (II) gave the bisamino-derivatives, (IV) and (V) (the latter may be a tautomer of the structure shown), unexpectedly of different structures:



Proof of mono- and disubstitution at the phosphazenyl-group again came from ^1H and ^{31}P n.m.r. spectroscopy. At ambient temperatures both the phosphazenyl- and phosphinyl-phosphorus n.m.r. signals of (V) showed coupling to an N*H*-proton (as demonstrated by ^1H decoupling). In view of the results for (III) (R = Bu^t), these could be two or four bond $P\cdots H$ couplings, with the former being most likely. There was no evidence of the formation of cyclic compounds of the type (VI)



(VI)

(R = Me or Bu^t) from reactions of (II) with three molar equivalents of amine; these compounds would be expected to show approximately equal coupling of the two ^{31}P nuclei to NMe or NBu^t protons. The stepwise addition of up to one molar equivalent of triethylamine to (III) (R = Me or Bu^t) resulted in small changes in ^{31}P n.m.r. parameters and finally a series of broad unidentifiable signals (R = Me), or recovery of starting material (R = Bu^t). Again, no evidence of (VI) was obtained. By contrast, compounds of the type $Cl_2P(X)\cdot NR\cdot P(X)NHR$ (X = lone pair or oxygen) are readily converted to cyclodiphosphazanes, $[Cl(X)PNR]_2$, under these conditions [8].

Lack of evidence for the formation of compounds (VI), and the literature reports [5, 6] leads us to believe that four-membered ring compounds containing a phosphazene linkage are difficult to obtain because the imposition of $P{=}\hat{N}{-}P$ bond angles of the order of 90° is energetically unfavourable. Although there is apparently little resistance to the opening of this angle to 180° [17], no crystal structures have been reported where it is less than *ca.* 120°.

The greater ease of nucleophilic displacement at phosphazenyl-, relative to the phosphoryl-, phosphorus atoms has also been demonstrated in the reactions of (II) with methanol [18], which initially gives $Cl_2P(O){\cdot}N{=}PCl_2(OMe)$. It is interesting that methylamine and t-butylamine effect geminal and non-geminal replacement of chlorine respectively. These observations might be anticipated by a simple consideration of steric effects, and indeed, nongeminal chlorine atom replacement by t-butylamine is observed [19] with $N_4P_4Cl_8$. However, these results can be contrasted with the geminal chlorine replacement by t-butylamine in $N_3P_3Cl_6$ and related six-membered ring compounds [1, 2].

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