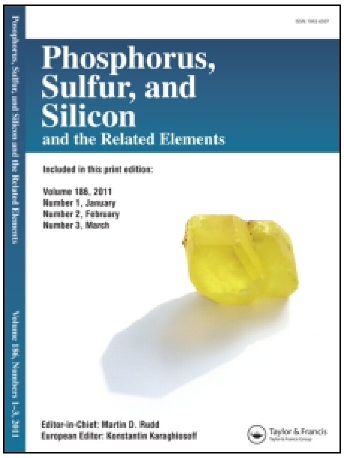

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^{31}P N.M.R. STUDIES OF THE REACTIONS OF LiN_3 WITH SOME ORGANOCHLOROPHOSPHORUS(V) COMPOUNDS

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^{31}P N.M.R. STUDIES OF THE REACTIONS OF LiN_3 WITH SOME ORGANOCHLOROPHOSPHORUS(V) COMPOUNDS

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Some new azido-derivatives of organochlorophosphonium(V) ions have been prepared in solution, and identified by means of ^{31}P n.m.r. spectroscopy. Attempts to substitute azide into organochlorophosphate(V) ions led to decomposition and the formation of phosphazene derivatives, however, and no new six-coordinate species could be detected.

Key words: Organochlorophosphorus($\bar{V}$) compounds; azide (reactions); ^{31}P-NMR.

Several fully-substituted azido-derivatives of organophophorus compounds are known,[1] yet it was not until 1978 that detailed n.m.r. studies of mixed azido-halogeno-species and their decomposition products were reported by Dillon et al.[2] Polymeric phosphazenes $(PBr_2N)_n$, $(PPhClN)_n$ and $(PPh_2N)_n$ have been synthesized by reacting NaN_3 with the corresponding phosphorus(III) halides at specific temperatures.[3] Photolysis with U.V. light between 195 and 206 K of HN_3 dissolved in PCl_3 gave a viscous liquid, with the stoichiometry $(P_5N_8Cl_9)_4$.[4] No evidence for the formation of azido-substituted phosphorus(III) compounds was found in either case, although PCl_2N_3 was considered as a likely intermediate in the formation of the tetramer. Dillon et al.[5,6] have identified the complete series of azido-chlorophosphates $[PCl_{6-n}(N_3)_n]^-$ in solution by ^{31}P n.m.r. spectroscopy, as well as the phosphorus(III) compounds $PX_{3-n}(N_3)_n$ (X = Cl or Br).[2] The azido-containing cations $[PMe_{4-n}(N_3)_n]^+$ $(1 \leq n \leq 3)$,[7,8] $[PMeCl_{3-n}(N_3)_n]^+$ and $[PPhCl_{3-n}(N_3)_n]^+$ $(1 \leq n \leq 3)$[9] have also been obtained in solution, and their ^{31}P chemical shifts recorded.[8,9] Other five- and six-coordinate azido-chloro-derivatives of phosphorus(V) compounds have been described by Skowronska et al.,[10] and by Dillon and co-workers.[9] In the present work we report the reactions of LiN_3 with some four- and six-coordinate organochlorophosphorus(V) species.

RESULTS AND DISCUSSION

(a) Substitution into Monoethyl- and Monophenyl-trichlorophosphonium Salts by N_3^-

When the salts $[PEtCl_3][SbCl_6]$ and $[PPhCl_3][SbCl_6]$ were treated separately with LiN_3 in $MeNO_2$ solution, new n.m.r. signals were observed upfield from those of

TABLE I

δ ^{31}P (p.p.m.) for $[PRCl_{3-n}(N_3)_n]^+$ ions in $MeNO_2$

R	n = 0	1	2	3
Et	128.9	92.0	62.9	51.6
Ph	103.3	72.6	51.6	35.5

the starting materials (Table I). These resonances were assigned to particular cationic species as shown. The chemical shifts for the phenyl derivatives are in good agreement with those recorded for the tetrachloroborate salt,[9] while the shift of 35.5 p.p.m. for the fully-substituted cation is in excellent agreement with the value reported by Buder and Schmidt.[8] When this solution was re-investigated after four days, the ^{31}P n.m.r. spectrum showed resonances at 103.3(w), 72.5(s), 51.6(m), 43.6(m), 32.4(w) and 21.1(w) p.p.m., the peaks at 43.6 and 21.1 p.p.m. arising from decomposition. The signal at 32.4 p.p.m. might also be due to a decomposition product, although it could originate from $[PPh(N_3)_3]^+$. The solution of $[PEtCl_{3-n}(N_3)_n]^+$ ions, on the other hand, gave a single resonance at 38.7 p.p.m. after four days, probably from the expected decomposition product $(PEt(Cl)N)_3$, or a related phosphazene.

(b) Substitution into $[PMe_2Cl_2][SbCl_6]$ and $[PEt_2Cl_2][SbCl_6]$ by N_3^-

When successive small amounts of LiN_3 were similarly added to solutions of $[PMe_2Cl_2][SbCl_6]$ or $[PEt_2Cl_2][SbCl_6]$ in $MeNO_2$, three peaks were observed in the ^{31}P n.m.r. in each case, which were readily assigned as indicated in Table II. The chemical shift for the cation $[PMe_2(N_3)_2]^+$ is in good agreement with the value reported by Buder and Schmidt.[8] With the addition of more azide, the ^{31}P n.m.r. solution spectrum of $[PEt_2Cl_2]^+$ showed a single resonance at 82.0 p.p.m., ascribed to the fully substituted cation $[PEt_2(N_3)_2]^+$. This shows that complete substitution of azide into the $[PEt_2Cl_2]^+$ cation can be achieved before any significant decom-

TABLE II

δ ^{31}P (p.p.m.) for $[PR_2Cl_{2-n}(N_3)_n]^+$ ions in $MeNO_2$

R	n = 0	1	2
Me	124.2	100.0	77.0
Et	138.7	108.0	82.2

position occurs. After four days a further upfield resonance at 64.5 p.p.m. was detected, besides the 82.0 p.p.m. peak; this was attributed to a decomposition product $(PEt_2N)_n$. When the $[PMe_2Cl_{2-n}(N_3)_n]^+$ system was monitored after five days, its ^{31}P n.m.r. spectrum showed two peaks, at 77.5(s) p.p.m., from the fully-substituted cation, and at 58.0(s) p.p.m., probably due to a polymeric phosphazene such as $(PMe_2N)_n$.

(c) *Reactions of* $PRCl_4$ *(R = Me or Et) with* N_3^-

When a small amount of LiN_3 was added to a solution of $PMeCl_4$ in $MeNO_2$, a vigorous reaction occurred. The reaction was left to subside, and the ^{31}P n.m.r. spectrum of the solution then recorded. Two resonances were observed at 53.3(s) and 43.6(m) p.p.m., assigned to the $[PMe(N_3)_3]^+$ ion[8,9] and a decomposition product. After a week the spectrum showed only two resonances at 42.0(s) and 29.1(w) p.p.m., ascribed to polyphosphazene decomposition products.

Addition of LiN_3 to a solution of $PEtCl_4$ in $MeNO_2$ was also accompanied by a vigorous reaction. The ^{31}P n.m.r. spectrum of the solution showed a set of four resonances, with shifts identical to those from the $[PEtCl_3][SbCl_6]$ reaction with LiN_3 (Table I), and readily assigned to the cations $[PEtCl_{3-n}(N_3)_n]^+$. When the spectrum was re-recorded after a week, resonances were observed at 59.6(s), 42.0(m), 25.8(m) and 6.5(w) p.p.m. These probably arise from polyphosphazene decomposition products, except for the signal at 59.6 p.p.m., which could be due to the $[PEtCl(N_3)_2]^+$ cation. The species giving a resonance at 42.0 p.p.m. is almost certainly identical to that giving a signal at 43.6 p.p.m. from decomposition of the $[PEtCl_{3-n}(N_3)_n]^+$ cations in the hexachloroantimonate (section a), though the minor signals differ in the two systems.

These phosphoranes are known to have the ionic structure $[PRCl_3]^+Cl^-$ (R = Me or Et) in the solid state,[13] so their similar behavior to that of $[PEtCl_3][SbCl_6]$ is not surprising. Reaction appears to be more rapid for the methyl than for the ethyl compound, since only the $[PMe(N_3)_3]^+$ cation was observed in the initial spectrum. Since the reactions were not carried out quantitatively, however, this difference could arise from relative concentration changes.

(d) *Reactions of* $[PRCl_5]^-$ *ions (R = Ph, Me or Et) with* N_3^-

These ions were prepared in situ by adding excess NR'_4Cl to a solution of the phosphorane $PRCl_4$ in CH_2Cl_2 or $MeNO_2$ until the "limiting shift" was attained.[14,17] When small amounts of LiN_3 were added to a solution of $[NEt_4][PPhCl_5]$ in CH_2Cl_2 or $MeNO_2$, rapid decomposition ensued, accompanied by the evolution of a colorless gas. The reaction was left to subside and the solution spectrum recorded; two resonances were observed, at 43.6 and 35.5 p.p.m. With more azide, other peaks were detected at 29.0 and 19.4 p.p.m. as well as the signal at 35.5 p.p.m., while the resonance at 43.6 p.p.m. was no longer present. The peak at 35.5 p.p.m. could be due to $[PPh(N_3)_3]^+$, and other signals are most probably from polyphosphazene decomposition products. Further addition of LiN_3 resulted in the appearance of new peaks to lower frequency, at 17.8, 12.9 and 9.8 p.p.m. When the solution spectrum was re-recorded the following day, the same number of peaks was apparent, with the same relative intensities. These peaks are in the expected region for phenyl-substituted cyclotriphosphazene derivatives.[18] The shifts are generally in good agreement with those of the decomposition products from $[PPhCl_{3-n}(N_3)_n]^+$ cations, except for the resonance at 9.8 p.p.m. which was not observed.[19]

Addition of LiN_3 to a solution of either $[PEtCl_5]^-$ or $[PMeCl_5]^-$ in $MeNO_2$ was accompanied by rapid decomposition. In the case of $[PEtCl_5]^-$, a single peak was observed at 38.7 p.p.m. in its ^{31}P n.m.r. spectrum, most probably from $(PEt(Cl)N)_3$ or a related phosphazene. After six days, three resonances at 38.7, 27.5 and 16.2 p.p.m. were detected, assumed to arise from polyphosphazene decomposition products. The $[PMeCl_5]^-$ solution initially showed two resonances, at 42.0 and 32.4 p.p.m. This solution was not investigated further.

There is no evidence for the formation of new six-coordinate azido-derivatives of $[PRCl_5]^-$ ions in any of these systems, unlike the reaction of $[PCl_6]^-$ with azide, where complete substitution up to $[P(N_3)_6]^-$ is possible.[5,6,15,16] Replacement of a chlorine by an organo-group thus seems to enhance the rate of decomposition of these species, in contrast with the relative kinetic stability in solution of the hexa-azidophosphate ion and its immediate precursor,[6,16] even though they are clearly very unstable from thermodynamic considerations.

EXPERIMENTAL

All manipulations including n.m.r. sample preparation were carried out either under an inert atmosphere of dry nitrogen or in vacuo. Chemicals of the best available commercial grade were used, in general without further purification, except for tetra-alkylammonium salts which were dried as described previously.[11] Lithium azide was prepared by the method of Hoffman-Bang.[12] Phosphorus-containing starting materials were synthesized as described in earlier publications.[13,14] In each instance a small amount of the compound under investigation was placed in an n.m.r. tube. A minimum amount of the requisite solvent was added, followed by cautious addition of the azide. For vigorous or violent reactions, the reaction was allowed to subside before sealing the tube and recording the solution ^{31}P n.m.r. spectrum. Isolation and further characterization of the azido-derivatives was not attempted because of their potential dangerously explosive nature.[15,16] ^{31}P n.m.r. spectra were recorded at 307.2 K as described previously.[6,14] Chemical shifts were measured relative to external 85% H_3PO_4, with the high frequency (downfield) direction taken as positive.

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