

Review

Isomerisations and tautomerism in phosphazene chemistry *

Robert A. Shaw

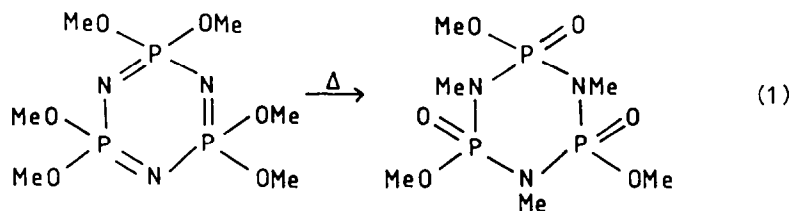
Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX (Great Britain)

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This brief review is intended to give a summary of irreversible and reversible migrations in cyclic and acyclic phosphazene derivatives.

O → *N* and *O* → *O* alkyl and *O* ⇌ *O* silyl group migrations

Historically, in 1961, the first of these migrations was the alkoxyphosphazene → oxo-*N*-alkylphosphazene rearrangement, observed for the cyclic esters $N_3P_3(OR)_6$ and $N_4P_4(OR)_8$ [1,2].

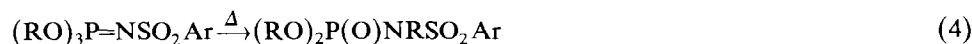


This occurred under the influence of heat (eq. 1) or of a catalyst (eq. 2).

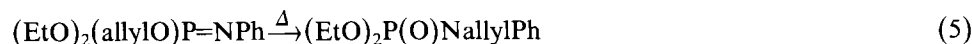
The haloalkane catalysed reaction of acyclic phosphazenes (eq. 3) was reported in the same year by Kabatschnik and Gilyarov [3], and in 1967 the thermal rearrange-



ment (eq. 4) was published by Kirsanov and co-workers [4] and by Pudovik and



co-workers (eq. 5) [5].



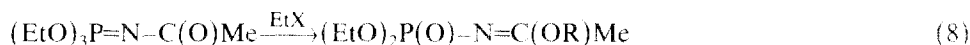
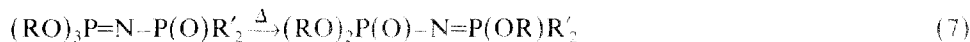
* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry.

More recently, this thermal rearrangement has attracted further attention [6,7]. The oligomeric series $\{\text{NP}(\text{OMe})_2\}_n$ ($n = 3, 4, 5$ or 6) was investigated using ^1H , ^{13}C and ^{31}P NMR spectroscopy. Some of the products have been crystallographically examined [8–10]. $\text{N}_3\text{P}_3(\text{OMe})_6$ gives only one (a *trans*) rearranged product. $\text{N}_3\text{Me}_3\text{P}_3(\text{O})_3(\text{OMe})_3$ [8]. $\text{N}_4\text{P}_4(\text{OMe})_6$ gives two derivatives. $\text{N}_4\text{Me}_4\text{P}_4(\text{O})_4(\text{OMe})_4$ [9,10]. The higher homologues, $\text{N}_5\text{P}_5(\text{OMe})_{10}$ and $\text{N}_6\text{P}_6(\text{OMe})_{12}$ also rearrange fully to give complex mixtures of isomeric products [6,7].

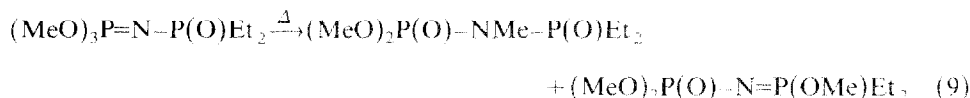
The phenylated derivative, $\text{N}_3\text{P}_3\text{Ph}_2(\text{OMe})_4$, also rearranges thermally to a mixture of fully and partially rearranged derivatives (eq. 6) [6,7].



In addition to $\text{O} \rightarrow \text{N}$ rearrangements, analogous $\text{O} \rightarrow \text{O}$ reactions, thermal (eq. 7, [11]) as well as catalytic (eq. 8, [12]) have been reported.



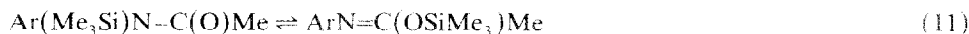
An example of a system with $\text{O} \rightarrow \text{N}$ and $\text{O} \rightarrow \text{O}$ migrations is due to Filatova et al. (eq. 9) [11]. Whilst alkyl group migration has attracted a good deal of attention,



silyl group migration has only been investigated more recently. Kabatschnik and co-workers [13], as well as Riesel and co-workers [14], investigated acyclic systems and obtained only evidence for a rapid $\text{O} \rightleftharpoons \text{O}$ exchange, but none for an $\text{O} \rightarrow \text{N}$ or $\text{O} \rightleftharpoons \text{N}$ exchange (eq. 10). The absence of $\text{O} \rightleftharpoons \text{N}$ silyl exchange in the phosphorus

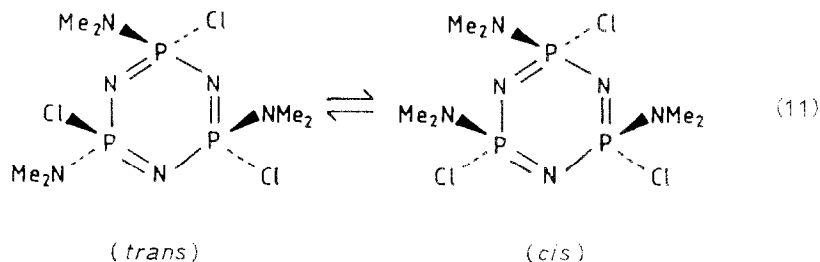


system contrasts with the ready exchange in an organic acid amide system (eq. 11) [15].



Cis \rightleftharpoons *trans* isomerisations

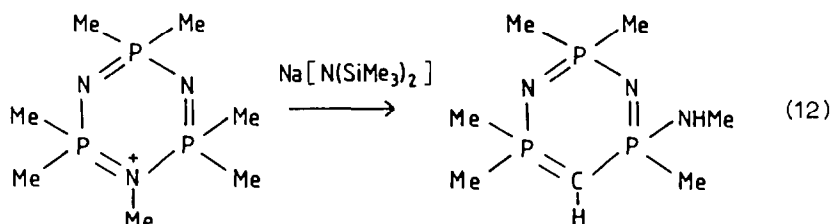
Nongeminal secondary, and to a lesser extent primary, amino derivatives of $\text{N}_3\text{P}_3\text{Cl}_6$ can undergo *cis* \rightleftharpoons *trans* isomerisation reactions at the bis-, tris- and tetrakis-amino stage. $\text{N}_3\text{P}_3\text{Cl}_{6-n}(\text{NR}_2)_n$ ($n = 2, 3$ or 4) (eq. 11).



Amine hydrochlorides, as well as aluminium(III) chloride, have been used as catalysts and these reactions can be of preparative value [16–18]. The equilibrium constants for such reactions have been reported [19].

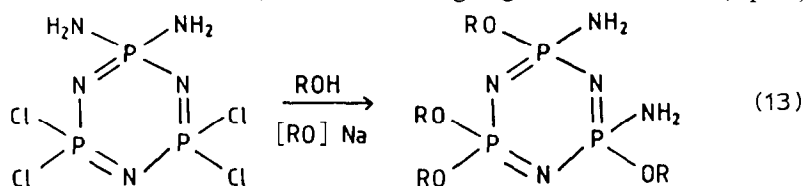
Phosphazene \rightarrow phosphorin rearrangements

An interesting phosphazene \rightarrow phosphorin rearrangement has been reported by Paddock and coworkers [20,21]. *N*-Methylphosphazanium iodides $N_nP_nMe_{2n+1}I$ ($n = 3$ or 4), on treatment with sodium bis(trimethylsilyl)amide, deprotonate and rearrange to phosphorin derivatives (eq. 12). The crystal structure of the rearranged trimer derivative has been published [22].



Geminal $\equiv P(\text{NH}_2)_2 \rightarrow$ nongeminal $\equiv P(\text{NH}_2)(\text{OR})$ migrations

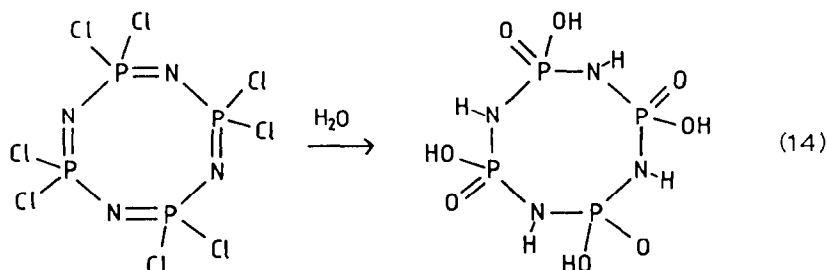
The most recently discovered rearrangement is that observed in the alcoholysis of $N_3P_3(\text{NH}_2)_2\text{Cl}_4$ [23]. The structure of the starting material had been controversial, until a recent crystal structure analysis proved its geminal nature [24]. This geminal diamide gives rise under the influence of alkoxide ions in alcohol to *cis*- and *trans*-nongeminal fully alcoholysed derivatives $N_3P_3(\text{NH}_2)_2(\text{OR})_4$, as well as, in the case of the methoxide, some unrearranged geminal derivative (eq. 13) [25].

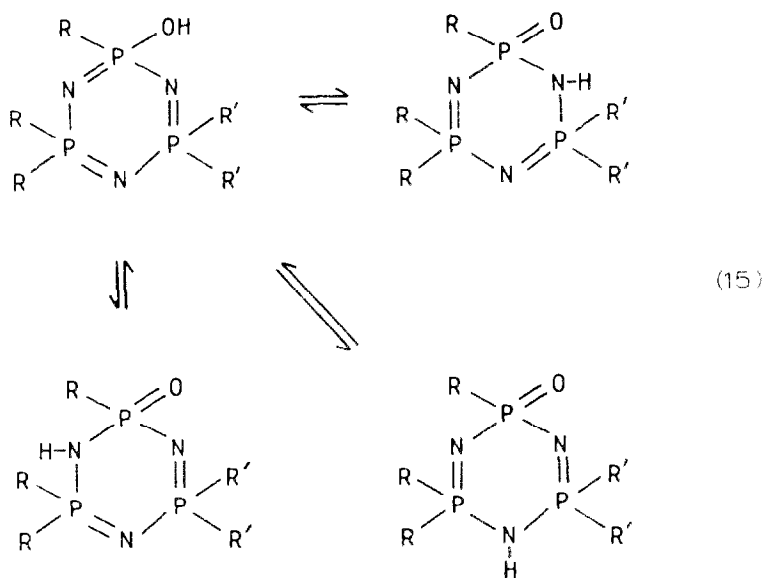


The *trans*- $N_3P_3(\text{NH}_2)_2(\text{OPr}^n)_4$, the *cis*- $N_3P_3(\text{NH}_2)_2(\text{OMe})_4$ and the geminal $N_3P_3(\text{NH}_2)_2(\text{OMe})_4$ have been crystallographically investigated [23,25].

Tautomerism

Tautomerism in phosphazene chemistry has a long history. It was recognised early, that hydrolysis of the chlorides, $(\text{NPCl}_2)_n$, gave rise not to dihydroxyphosphazenes, but to hydroxyoxophosphazanes (eq. 14) [26]. Crystallographic evidence of this tautomerism has been presented [27,28].



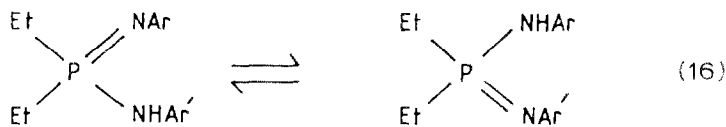


One question, however, remained unanswered in the above studies, namely, whether the $O \rightarrow N$ tautomerism involved migration of a proton from oxygen to a nitrogen α or γ to the phosphoryl group (eq. 15).

Recent work on "monohydroxy" derivatives, e.g. $N_3P_3R_5OH$, has shown that in all cases so far investigated, the proton migrates to the α -ring nitrogen atom [29,30]. Variable temperature ^{31}P NMR spectroscopy is an excellent tool to investigate this phenomenon: three types of tautomerism involving α -nitrogen atoms were postulated and experimentally observed [30]. These were related to nitrogen basicities: (i) one site much more basic than the other, no $N \rightleftharpoons N$ tautomerism observable, and the ^{31}P NMR spectrum (ABX) is temperature invariable; (ii) two equivalent sites, rapid exchange between them gives rise to an A_2X spectrum, slow exchange to an ABX spectrum; (iii) two nonequivalent sites, in the fast exchange limit this gives an ABX spectrum, whilst in the slow exchange limit two ABX spectra can be observed [30]. Crystal structure data is now available for one example from every one of these three classes [29,31,32].

The tautomerism was related to the basicity behaviour of phosphazenes and it was shown that a knowledge of the latter can be used to predict and calculate tautomeric behaviour [30,33].

Kabatschnik and coworkers have carried out major studies on acyclic phosphazenes [34], no evidence for $N \rightleftharpoons O$ tautomerism was detected by IR spectroscopy. $N \rightleftharpoons N$ tautomerism in monomeric phosphazenes was, however, amply documented (eq. 16).



Our researches on these topics continue. We are currently investigating under which conditions $\equiv\text{P}(\text{NH}_2)_2$ react with or without migration, and also whether other groups such as NHR can be induced to similar behaviour [35].

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