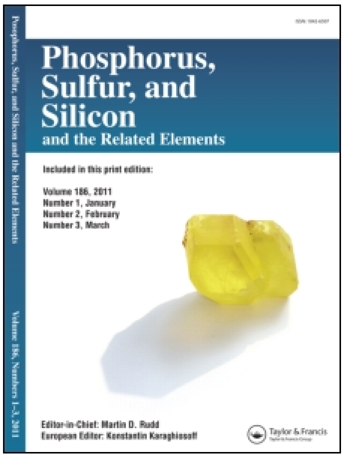

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Mechanisms of Formation of the Cyclodiphosphazane and Cyclotriphosphazane Ring Systems

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To cite this Article Murray, M. and Woodward, G.(1989) 'Mechanisms of Formation of the Cyclodiphosphazane and Cyclotriphosphazane Ring Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 3, 399 — 403
To link to this Article: DOI: 10.1080/10426508908039730
URL: http://dx.doi.org/10.1080/10426508908039730

Phosphorus, Sulfur and Silica, Vol. 41, pp. 399–403
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MECHANISMS OF FORMATION OF THE CYCLODIPHOSPHAZANE AND CYCLOTRIPHOSPHAZANE RING SYSTEMS.

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Abstract Four- and six-membered phosphorus(V) nitrogen ring compounds have been prepared from phosphorus(V) halides and amides, and their structures determined by n.m.r, mass spectroscopy and X-ray crystallography. The role of three-coordinated intermediates is discussed.

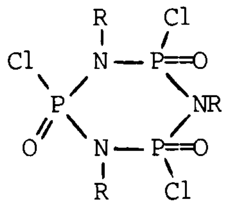
INTRODUCTION

In phosphorus(V) chemistry, cyclophosphazanes, containing phosphorus-nitrogen single bonds, are far less well known than the cyclophosphazenes, or phosphonitriles, which contain double bonds. Also, most of the reported cyclophosphazanes have four-membered rings, whereas cyclophosphazenes always have six or more atoms in the ring. Michaelis [1] reported the preparation of a four-membered ring compound $[PhNPOCl]_2$ by heating aniline hydrochloride with equimolar amounts of phosphorus oxychloride. The initial product of the reaction is $PhNHPOCl_2$, which loses HCl on further heating. Michaelis´ product had M.Pt. 223° and was water stable. Hopkins, Green, and Haszeldine [2] prepared the compound by reacting the four-membered ring compound $[PhNPCl_3]_2$ with SO_2 and reported a M.Pt. of 143-145°. Their product was extremely water-sensitive, and showed two peaks in the ^{31}P n.m.r. spectrum, as would be expected for the two possible isomers (cis and trans).

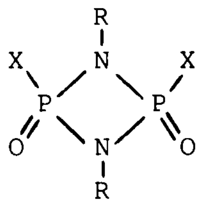
RESULTS

We have repeated Michaelis′ reaction and proved that his product is in fact the trimer, $[PhNPOCl]_3$ (I, R, R′ = Ph) [3]. If the $POCl_3$ and aniline hydrochloride are in strictly equimolar proportions no dimers are observed. The trimer exists as two isomers, the major, asymmetric isomer giving an AB_2 ^{31}P n.m.r. spectrum, while the minor, symmetric isomer gives a singlet, as all three phosphorus atoms are chemically equivalent. These structures have been confirmed by mass spectroscopy and X-ray crystallography. The latter shows that the six-membered rings exist as twisted boats, and that the nitrogen atoms are essentially planar. However, the phenyl rings are perpendicular to the planes of the nitrogen atoms, presumably due to steric hindrance.

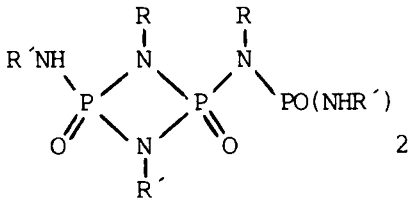
We have also succeeded in preparing the 3-methylphenyl, 4-methylphenyl, and 4-methoxyphenyl analogues, but were unable to prepare any simple alkyl analogues (R = Me, Et, iBu etc.). Since the four primary amines from which we were able to prepare the cyclotriphosphazanes all have a pK_a near 5, we looked for an aliphatic amine with a similar pK_a. 2,2,2-Trifluoroethylamine, $CF_3CH_2NH_2$, has a pK_a of 5.84, and reaction of its hydrochloride with $POCl_3$ indeed yielded the cyclotriphosphazane I (R, R′ = CH_2CF_3).



I



II

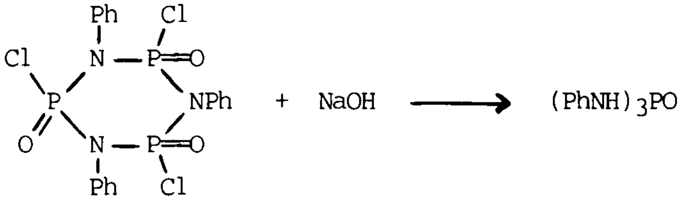


III

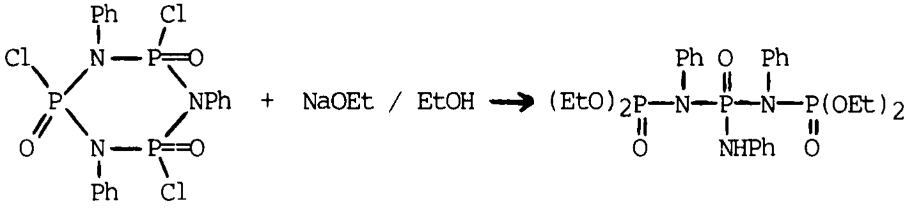
Looking for alternative routes to alkyl derivatives of I we prepared the chain compound $POCl(MeNPOCl_2)_2$ which we hoped would form compounds of type I on reaction with primary amines. However, reaction with iso-butylamine produced the four-membered ring derivative III (R = Me, R′ = iBu), and the reaction with methylamine initially formed a similar compound, but the four-membered ring was then cleaved by methylamine to form the aminolysed chain compound $MeNHPO[MeNPO(NHMe)_2]_2$. Only on reaction with aniline hydrochloride were we able to observe traces of the cyclotriphosphazane I (R = Me, R′ = Ph).

Thermolysis of phosphoric acid triamides, $(RNH)_3PO$, has been reported [4] to yield cyclodiphosphazanes (II, X = NHR). We have confirmed this reaction for R = iBu and Ph, and in both reactions we identified $RN[PO(NHR)_2]_2$ (IV) as a side-product. When R = Me no identifiable products could be obtained (cf. [5]). This again suggests that methylamine is able to cleave the four-membered ring.

All the cyclotriphosphazanes we have prepared are relatively inert towards nucleophiles. They do not react with water or amines at room temperature. Heating I (R, R′ = Ph) with piperidine hydrochloride yields a cyclodiphosphazane, II (R = Ph, X = piperidyl), and with stronger nucleophiles (OH^-, OEt^-) the products obtained (see reactions I and II) suggest that ring contraction to products like III may have occurred, followed by cleavage of the rings.



Reaction I



Reaction II

DISCUSSION

The importance of amine basicity in determining the products of the reactions allows us to draw certain conclusions about the mechanisms of the reactions we have studied. Loss of HCl from $RNHPOCl_2$ may proceed either unimolecularly, to produce the three co-ordinate species RN=POCl, or bimolecularly, to form $RNHPOClNRPOCl_2$ (V). The three-coordinate species, if it is formed, would be very reactive, so would probably react with $RNHPOCl_2$ to form (V) rather than dimerise to form II, and we have n.m.r evidence for the presence of (V) in the case when R = Ph. Further reaction of (V) could then form a longer chain P-N-P-N-P, which with less basic amines, e.g. aniline, will lose HCl to form the six-membered ring product. With more basic amines, e.g. primary alkylamines, such chains will react to form four-membered rings rather than six-membered rings, as shown above. The steric crowding evident in the cyclotriphosphazanes from the unusual configuration of the phenyl rings also makes the six-membered rings more difficult to form, and this steric crowding is probably a contributory factor to the ring contraction observed in the reactions of the cyclotriphosphazanes with nucleophiles.

In the thermolysis reactions of the triamides $(RNH)_3PO$ the three-coordinate species RNHPONR appears to be less reactive towards the starting material, so that sufficient concentrations can build up for dimerisation to occur. Some reaction with the triamide may occur to give (IV), but this is not readily converted to the cyclodiphosphazane; indeed, it may be a product of reaction of the released amine with the cyclodiphosphazane. Further reaction via the route followed by the halides is prevented by the inertness of (IV), and in none of the thermolysis reactions were six-membered rings ever observed.

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