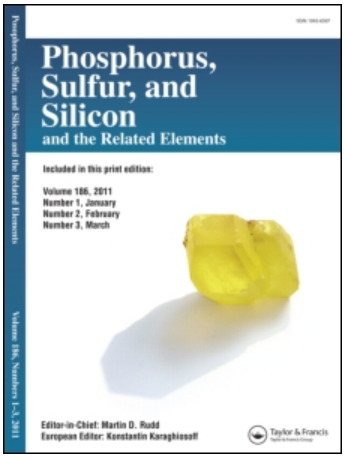

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Steric Congestion and Reactivity in Cyclophosphazanes

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STERIC CONGESTION AND REACTIVITY IN CYCLOPHOSPHAZANES

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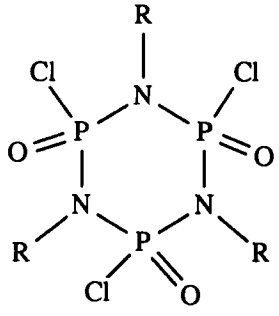
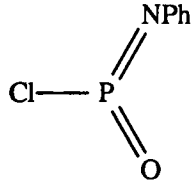
We have already demonstrated [1] that the cyclotriphosphazane (**1**) is produced in the reaction of phosphorus oxychloride, $POCl_3$, with aniline hydrochloride. The formation of the trimer is proof that dimerisation of a three-coordinated, λ^5-phosphorus species, e.g. (**2**), is not occurring. The principal isomer of (**1**) formed is the trans form (**1a**), but small amounts of the cis form, (**1b**), are also formed. Crystal structures of both isomers have now been determined, and



(**1a**) R = Ph, *trans*

(**1b**) R = Ph, *cis*

(**1c**) R = 3-MeC_6H_4



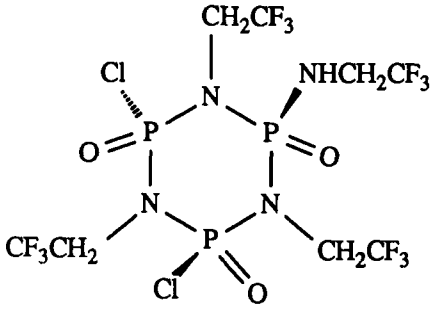
(**2**)

show that the ring exists as a twisted boat in (**1a**) and as almost planar twisted chair and boat in the two crystallographic forms of (**1b**). The nitrogen atoms are planar, as is usual in P(V)-N compounds, but the planes of the nitrogen atoms are not coincident with the planes of the attached phenyl rings.

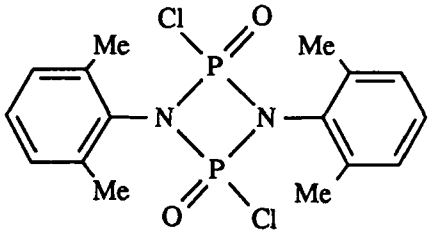
Although the orientation of the phenyl rings in (**1**) is indicative of a certain

amount of steric congestion, it is apparent that the main influence governing the formation of (1) or derivatives is the basicity of the amine RNH_2 from which the compounds are derived. Thus we have discovered that cyclotriphosphazanes are only formed from amines with a pK_a between 4.5 and 6.0, which largely restricts the reaction to aromatic amines, e.g. $C_6H_5NH_2$, 3-$MeC_6H_4NH_2$, 4-$MeC_6H_4NH_2$, and 4-$MeOC_6H_4NH_2$; the only aliphatic amine we have found that will form a cyclotriphosphazane is $CF_3CH_2NH_2$, which has a pK_a of 5.84. Although we do not have a crystal structure of this cyclophosphazane, two observations suggest that the structure may be slightly influenced by the smaller CF_3CH_2 group attached to nitrogen. These are the much larger difference in the chemical shifts of the two different kinds of phosphorus nuclei in the cyclophosphazane, and the formation of an amino substituted derivative (3) of a type which has not been observed for the aromatic derivatives.

For the aromatic derivatives, the perpendicular orientation of the phenyl



(3)



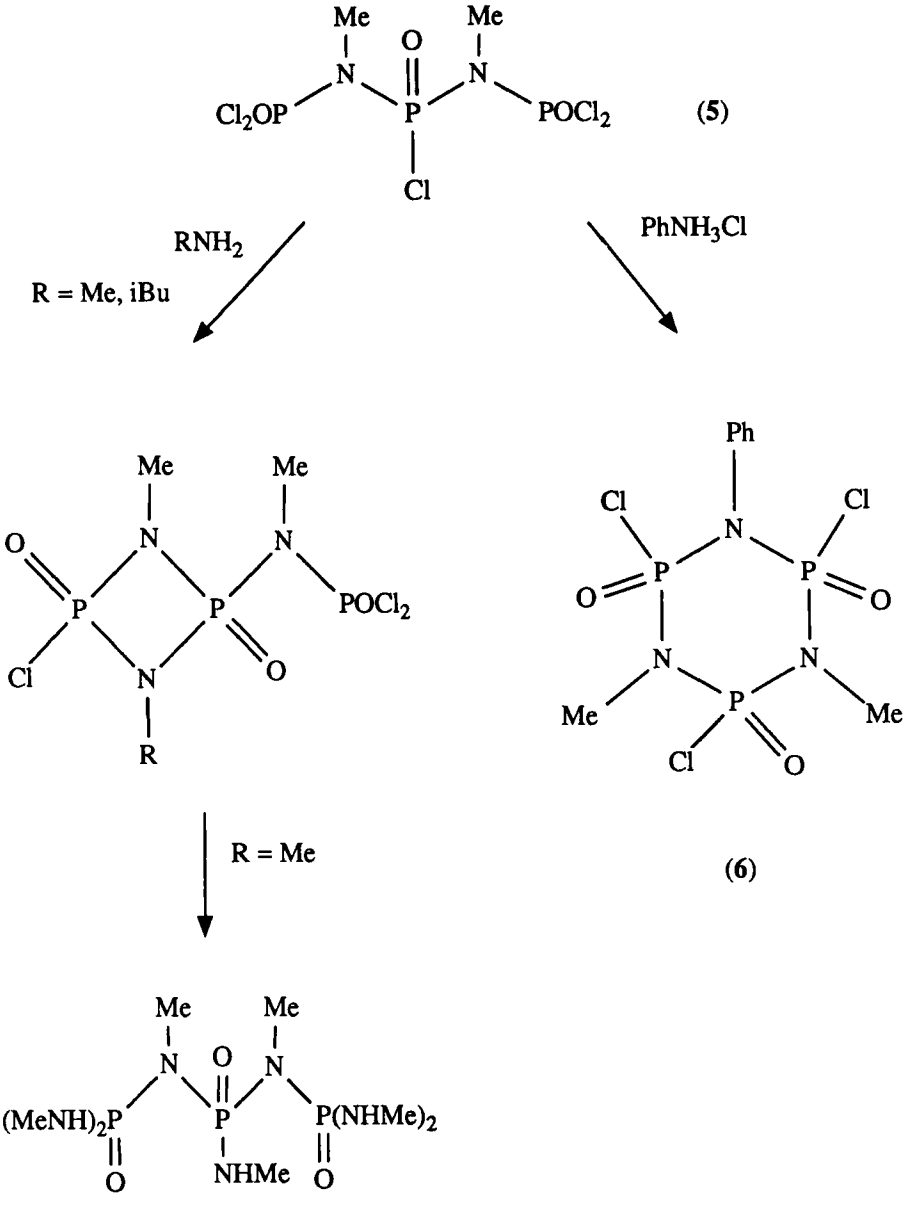
(4)

rings with respect to the plane of the nitrogen atoms has a strong influence on the ^{13}C n.m.r. shifts of the aromatic rings. Thus for both isomers of (1) all the ^{13}C signals occur in the range 130 to 133 ppm, whereas in $C_6H_5NHPOCl_2$ the C-2 and C-4 carbons have shifts of 119 and 123 ppm respectively. The shifts thus provide a sensitive probe of the orientation of phenyl rings in phosphorus-nitrogen compounds, which can be divided into two classes as below.

Class 1 (Coplanar Ar-N)	Class 2 (Orthogonal Ar-N)
$ArNHPOCl_2$	$ArN(POCl_2)_2$
$(ArNH)_3PO$	$[ArNPOCl]_3$
$[ArNPOX]_2$	$[2,6\text{-}Me_2C_6H_3NPOCl]_2$
	$[ArNPCl_3]_2$

A consequence of the orthogonal orientation of the phenyl groups in cyclotriphosphazanes is that non-equivalence of the ortho- and meta-carbons of the phenyl rings is expected if rotation is slow enough. This is observed on cooling (**1a**) or (**1b**) to -70°. Similarly, the ^{31}P n.m.r. spectra of (**1c**) shows the presence of several isomers due to the different orientation of the asymmetric phenyl rings, and the cis isomer of (**4**) shows two types of methyl groups corresponding to the two different sides of the four-membered ring.

The orthogonal orientation of the phenyl rings is a clear indication of steric congestion, and it is therefore hardly surprising that the reactions of cyclotriphosphazanes show some deviation from those of typical acyclic derivatives. Thus we have not been able to carry out any simple substitution reactions at phosphorus; weak nucleophiles, such as water and amines, have no effect on the ring compounds, while stronger nucleophiles, such as OH^- and OEt^- lead to interesting ring contraction reactions, the products being $(PhNH)_3PO$ and $PhNHPO(NPhPO(OEt)_2)_2$ respectively. The reason for these ring contraction reactions is probably the difficulty of accommodating the five-coordinated transition state of the $s_N2(P)$ substitution reaction in a six-membered ring. This instability of the six-membered phosphorus nitrogen ring system towards stronger nucleophiles is obviously the reason for the dependence of its formation on amine basicity, more basic amines, e.g. methylamine and ethylamine, being able to cleave any rings that might be formed. The effect of amine basicity is again seen in the reactions of the linear phosphazane (**5**) which gives, at least initially, four-membered ring products

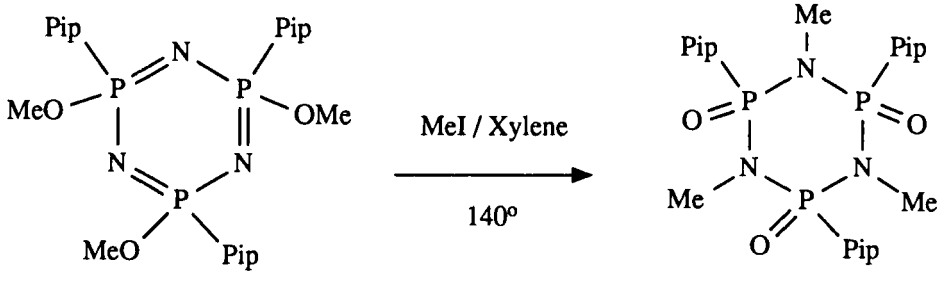


with more basic amines, and only gives small amounts of the cyclotriphosphazane (**6**) on reaction with aniline hydrochloride. Similarly, the reactions of (**1a**) with

aniline or piperidine hydrochlorides, while leading to substitution of the chlorines by amino groups, are also accompanied by ring contraction, the products being amino substituted diphosphetidines.

Although it is not possible to make amino substituted cyclotriphoshazanes by substitution reactions, and direct synthesis of N-methyl substituted cyclotriphosphazanes is similarly impossible, we have shown that amino substituted N-methyl cyclotriphosphazanes are quite stable compounds by the synthesis of (**7**) by the following scheme. The phosphazene-phosphazane rearrangement, catalysed by methyl iodide, proceeds smoothly in refluxing xylene.

In syntheses of the cyclotriphosphazanes we noticed two triplets in the ^{31}P

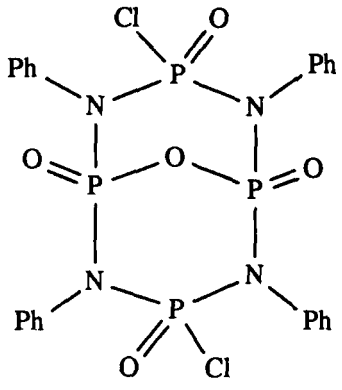


Trans isomer

(**7**) Trans isomer

n.m.r. of the reaction mixture, which must be due to a tetraphosphorus compound. It cannot be the tetramer, $[PhNPOCl]_4$, since none of the isomers of this compound would have an A_2X_2 spin system. Isolation of the product proved that it was the bicyclic derivative (**8**), which has arisen from water impurities in the reaction mixture, which presumably form $P_2O_3Cl_4$. Deliberate addition of water to the reaction mixture leads to substantially increased yields of (**8**), and similar addition of $PhN(POCl_2)_2$ to the reaction mixture gives the related product (**9**). Crystal structures of both these compounds have been determined, and again all the phenyl rings are orthogonal to the planes of the nitrogen atoms to which they are attached.

Although cleavage of the P-O-P bridge of (**8**) to give cyclotetraphosphazanes is possible, the reactivity of the products is again influenced by the steric congestion of the phenyl rings at the nitrogens, so it has not been possible to make the



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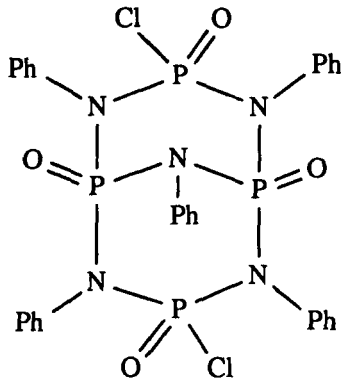

(9)

eight-membered product $[PhNPOCl]_4$ by this route.

(1) O.Johnson, M.Murray, and G. Woodward, J. Chem. Soc. (Dalton), 1989, 821