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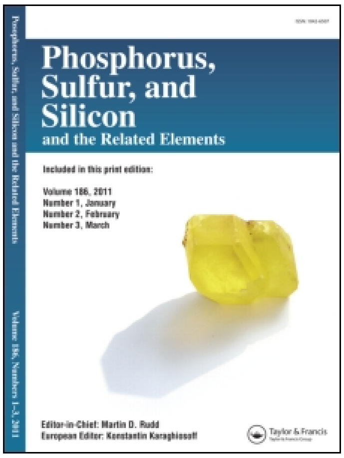

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NMR Studies of Hydrolysis and Rearrangement Reactions of Cyclophosphazenes

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NMR STUDIES OF HYDROLYSIS AND REARRANGEMENT REACTIONS OF CYCLOPHOSPHAZENES

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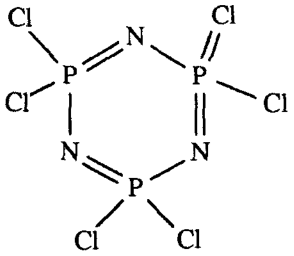
We have studied the controlled hydrolysis of $P_3N_3Cl_6$ (**A**) under basic conditions (Et_3N/H_2O in $CDCl_3$) by ^{31}P n.m.r. Our results are in some respects at variance with those reported in acid conditions by Gabler and Haw[1], but agree better with results of van de Grampel *et al.*[2,3] The first species observed (**I**) we assign structure **B**, and our data agree well with those of van de Grampel *et al.*[2], who isolated salts containing the anion. Gabler and Haw[1] quote a higher coupling constant and a higher shift for the PClO phosphorus, but this can be explained by the more acid conditions they used. Species such as **B** exist as an equilibrium of anionic and tautomeric O- and N-protonated structures. Further hydrolysis gives rise to four more species, two A_2X systems, **II** and **III**, and two P-O-P bridged species, one symmetrical $[A_2X]_2$ system **IV**, and one asymmetrical A_2XYB_2 system **V**. The symmetrical system **IV**, whose second order spectrum clearly shows the effect of the P-O-P coupling, cannot be **C**, for which an X-ray crystal structure has been reported by van de Grampel *et al.*[3] (δ_{PCl2} 21.5, δ_{PClO} 2.3, $J_{PNP} \sim 70$ Hz, J_{POP} not reported). **IV** is almost certainly **D**, or its tautomer **E**; the high value of J_{PNP} (55 Hz) suggests it is a neutral molecule, and **E** would exist as the anion in the basic conditions. The correspondence of the n.m.r. data of the two rings in **V** with the data for **C** and **D** strongly suggest that **V** is **F**.

Table 1. ^{31}P n.m.r data for species observed in Hydrolysis of A

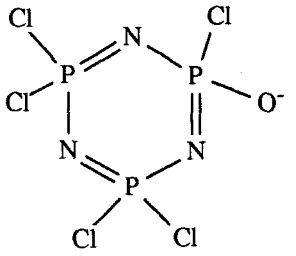
Species	δ_{PCl2}	δ_{PO}	J_{PNP}	J_{POP}	Assignment
I	20.3	-0.4	44		**B**
II	20.8	2.5	44		**?**
III	11.1	-9.8	37		**G?**
IV	18.0	-14.9	55	22	**D**
V	21.7	0.3	69	28	**F**
	20.6	-13.6	59	28	

The two A_2X systems (other than **I**) observed (**II** and **III**) correspond (though with different coupling constants and, especially in the case of **III**, different chemical shifts) to two species observed by Gabler and Haw[1], and assigned by them as **G** and **D**. We have shown above that **D** has quite different n.m.r. data, and, as they say, "it is difficult to imagine an additional monomeric hydrolysis product with n.m.r. properties similar to **B** and **G**". The similarity of the shift of the triplet of **III** (-9.8) to the shifts of the PO_2 groups in **IV** and **V** suggests to us that **III** may be **G**, but leaves open the identity of **II**.

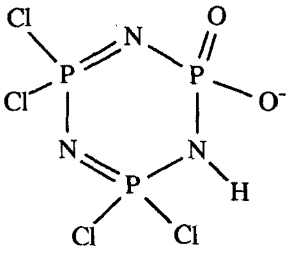
The observation of **G** (**II** or **III**) shows that geminal di-substitution is occurring, but we can see no evidence for any of the possible products of vicinal disubstitution, although such species were observed by both Gabler and Haw[1] and by van de Grampel *et al.*[2], admittedly under somewhat different conditions.



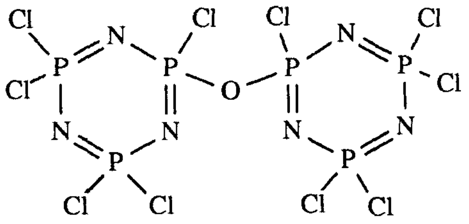
A



B



G



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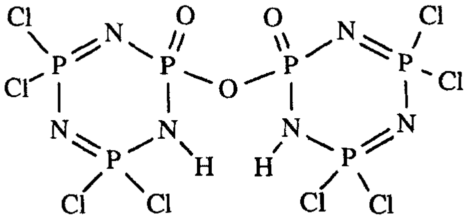
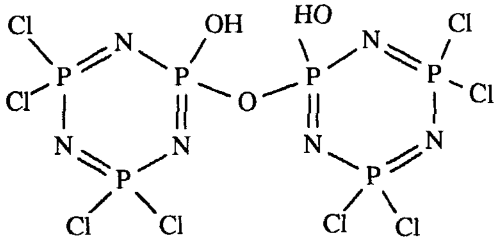
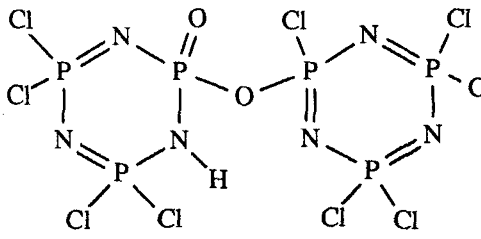


D



E



F

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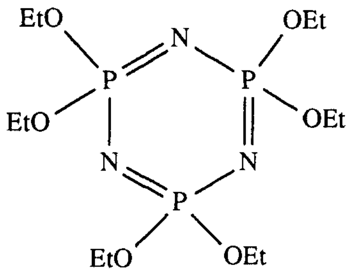
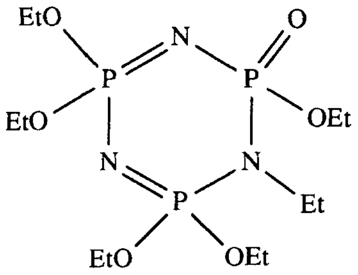
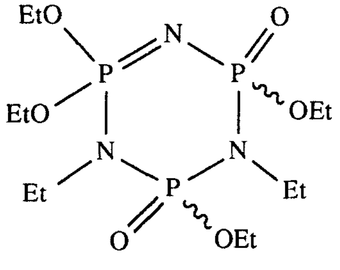
Further hydrolysis of **A** yields trimetaphosphimic acid, $(HNP(=O)OH)_3$, the silver salt of which was shown by Rätz and Hess[4] to react with ethyl iodide, producing a product they claimed was **Z**. In the course of our studies on phosphazane oxides[5] we repeated the reaction; ^{31}P n.m.r. of the chloroform-soluble products obtained after 4 hours reaction at 100° in a sealed tube showed the presence of three major products, which can be assigned as **W**, **X**, and **cis-Y**. The appearance of these products shows that ethyl iodide attacks principally at oxygen, not nitrogen, and that the initial product of the reaction is therefore **W**. We tested the theory that **X** and **Y** are the result of a phosphazene-phosphazane rearrangement[6] by repeating the reaction with a 12 hour reaction period and using excess ethyl iodide. The product of this reaction was principally **cis-Y**, with smaller amounts of **trans-Y**, **cis-Z**, and **trans-Z**.



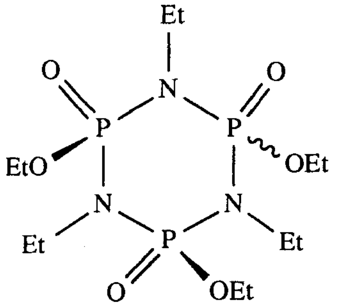
W



X



Y



Z

Assignments of individual resonances, as well as the structural assignments, were largely based on magnitudes of P-P coupling constants, which show a fairly consistent pattern, and are presented in the Table. The two types of phosphorus atom, P=N and P=O, can be connected either by double-bonded (phosphazene) nitrogen or by single bonded (phosphazane) NEt. Typical coupling constants for the four observed situations are

-P=N-P=N	75
-P=N-P=O	50-62
O=P-NEt-P=N	37-48
O=P-NEt-P=O	22 (cis) or 27 (trans)

Although the ^{31}P chemical shifts show a general downward trend from phosphazene to phosphazane, there are too many variations to allow them to be used as aids in assignment.

The observation of a phosphazene-phosphazane rearrangement with POEt compounds is in contrast to the results of Krishnamurthy *et al.*[6], though may be explained by our use of a large excess of ethyl iodide to catalyse the reaction. However, we could not get the rearrangement to go to completion, **Y** being the major product rather than **Z**.

Table 2. ^{31}P n.m.r. data for isomers of $P_3N_3(OEt)_6$

Compound	δ_{PA}	δ_{PB}	δ_{PC}	J_{AB}	J_{AC}	J_{BC}
W	17.46	17.46	17.46	n.m.	n.m.	n.m.
X	14.97	7.97	1.40	75	48	58
cis-Y	9.80	3.05	-3.22	37	22	62
trans-Y	9.42	2.40	-3.55	38	28	50
cis-Z	4.35	4.35	4.35	n.m.	n.m.	n.m.
trans-Z	7.32	5.21	5.21	25	25	n.m.

Underlined shifts refer to P=N groups.
n.m. indicates coupling constants not measured

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