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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>

Synthesis and Crystal Structure of a New Class of Oxygen Bridged Bicyclic Tetraphosphazanes

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To cite this Article Murray, M. and Woodward, G.(1990) 'Synthesis and Crystal Structure of a New Class of Oxygen Bridged Bicyclic Tetraphosphazanes', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 476

To link to this Article: DOI: 10.1080/10426509008041000

URL: <http://dx.doi.org/10.1080/10426509008041000>

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SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW CLASS OF OXYGEN BRIDGED BICYCLIC TETRAPHOSPHAZANES

M. MURRAY, G. WOODWARD

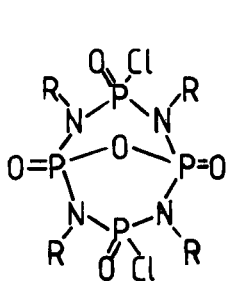
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The reaction of primary amine hydrochlorides with phosphorus oxychloride in the presence of 1/4 mole of H_2O yields the title compounds I ($R = C_6H_5-$, $4-CH_3C_6H_4-$, $4-CH_3OC_6H_4-$, $3-CH_3C_6H_4-$, CF_3CH_2-). Hydrochlorides of more basic amines do not yield any cyclic material. The compound I ($R = C_6H_5$) was isolated as one isomer.

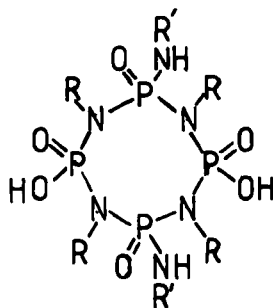
An X-ray crystallographic study has shown an open ring structure in which the two chlorine atoms are positioned on the same face of the P_4N_4 ring as the P-O-P bridge.

An initial study of the reactivity of this ring system has shown similarities to that of $[C_6H_5NPOCl]_3$. The P-O-P bridge can be selectively hydrolysed, e.g. H_2O /primary aliphatic amine yields compounds of type II, but reaction with stronger nucleophiles such as sodium ethoxide in ethanol yields polymeric material.

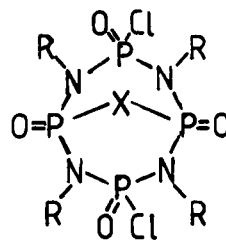
This chemistry could provide a useful route to cyclotetraphosphazane ring systems and may also yield new bicyclic ring systems e.g. III.



(I)



(II)



(III)

($R = \text{aryl}$, $R' = \text{alkyl}$, $X = CH_2$ or NR')