

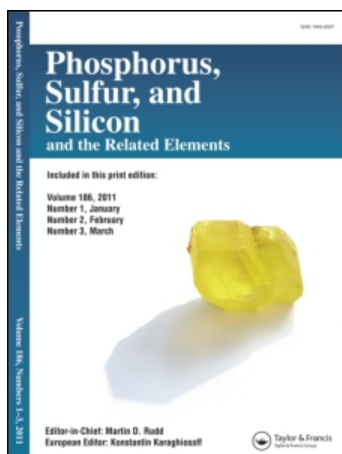
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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Cyclic Phosphorus(V) Compounds: Phosphazanes and Anhydrides

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## Cyclic Phosphorus(V) Compounds: Phosphazanes and Anhydrides

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$^{31}\text{P}$  n.m.r. has been extensively used to study the preparation and reactions of cyclic phosphorus-(V) compounds containing P-N-P and P-O-P linkages. Michaelis' "Oxyphosphazobenzolchlorid",  $[\text{C}_6\text{H}_5\text{NPOCl}]_n$  has been shown by  $^{31}\text{P}$  n.m.r. and mass spectroscopy to be the trimer ( $n=3$ ), not the dimer as proposed by Michaelis. The competing reactions of aniline hydrochloride and  $\text{POCl}_3$  to form the dimer (two isomers cis- and trans-) and the trimer have been elucidated. With  $\text{PSCl}_3$  only the dimer  $[\text{C}_6\text{H}_5\text{NPSCl}]_2$  is formed (both isomers).

The reaction of  $\text{RPOCl}_2$  with one mole of water in the presence of triethylamine has been shown to yield the dimer  $[\text{RPO}_2]_2$  (one isomer only) if  $\text{R} = \text{C}_6\text{H}_5$  and the trimer  $[\text{RPO}_2]_3$  if  $\text{R} = \text{Et}_2\text{N}$ , whereas the reaction of  $\text{C}_6\text{H}_5\text{POCl}_2$  with  $\text{C}_6\text{H}_5\text{PO}(\text{OH})_2$  yields principally the trimer with no trace of dimer.

All the six-membered ring compounds studied have been shown to have the "two up, one down" arrangement of ligands at the three phosphorus atoms, no evidence having been found for the symmetrical structure, although a crystal structure of the symmetrical isomer of  $[\text{Et}_2\text{NPO}_2]_3$  has been reported without details of its preparation.

An initial study of the reaction of  $[\text{C}_6\text{H}_5\text{NPOCl}]_3$  with  $\text{NaOEt}$  has produced a remarkable rearrangement to form  $[(\text{EtO})_2\text{PONC}_6\text{H}_5]_2\text{PONHC}_6\text{H}_5$ .