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New Cyclic Phosphorus Compounds from the Partial Nucleo-Philic Degradation of Phosphorus(III) Oxide - A NMR Study

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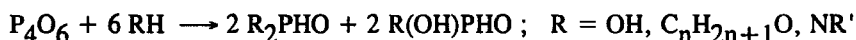
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NEW CYCLIC PHOSPHORUS COMPOUNDS FROM THE PARTIAL NUCLEOPHILIC DEGRADATION OF PHOSPHORUS(III) OXIDE - A NMR STUDY

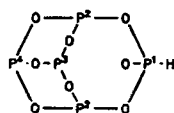
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Abstract On the reaction of P_4O_6 with small amounts of water new cyclic compounds are formed apart from polymeric solid containing P(III)- and P(V)-phosphorus. A possible path of formation of the rings is discussed.

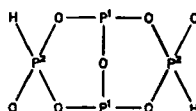
The reaction of phosphorus(III) oxide with an excess of protic nucleophiles like water, alcohols or amines leads to an equimolar mixture of the corresponding mono- and disubstituted phosphonic acids:



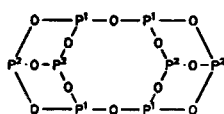
With very small amounts of water or ethanol in solvents like dioxan or chloroform as main product an insoluble polymeric phosphorus oxide is formed. In the supernatant solvent besides P_4O_6 and P_4O_7 by a detailed NMR spectroscopic study some new cyclic compounds containing trivalent phosphorus have been identified by comparison of the observed and the simulated spectra. The new compounds were observed in only very low concentrations relative to the total amount of phosphorus. In the following scheme the constitutional formulae are given:



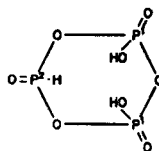
$H_2P_2O_6$



$H_2P_2O_7$



P_8O_{12}



$H_3P_3O_9$

The $\text{H}_3\text{P}_3\text{O}_8$ -molecule is formed on hydrolysis of a phosphorus(III/V) oxide with an approximate composition P_4O_9 .

The formation of the observed new cyclic compounds can be explained by alternating hydrolysis and condensation steps. One possible path of formation of some of the new cycles is given in the following scheme:

