Some Thermal Condensation Reactions of Phenylphosphonothioic Diamides. A New Phosphorus–Nitrogen–Sulphur Heterocyclic System

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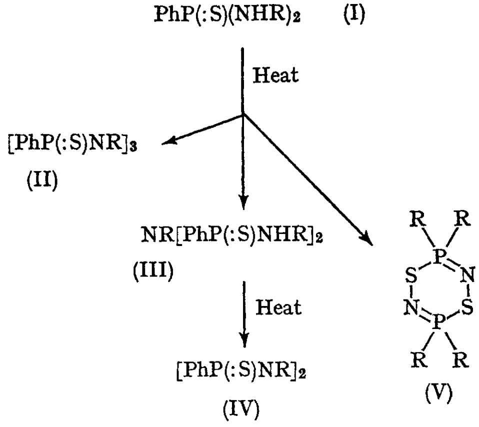
IN connection with polymerisation studies on phenylphosphonic[1] and phenylphosphonothioic diamides[2] more detailed investigations into the behaviour of the relevant monomers and oligomers became necessary. We report here on the sulphur-containing species. Apart from a study by Trippett[3] on the thermal condensation dimerisation of two diamides, $PhP(:S)(NHR)_2$ (I; R = Me or CH_2Ph), nothing definite is known about the behaviour of this class of compounds.



We have prepared a series of monomeric diamides, $PhP(:S)(NHR)_2$ (I; R = H, Me, Et, Pr^n, Bu^n, or Ph) and have studied their thermal condensation reactions. The parent diamide (I; R = H) condenses near 160° to the cyclic trimer $[PhP(:S)NR]_3$ (II; R = H) whilst most of its alkyl homologues so far studied give the cyclic dimers $[PhP(:S)NR]_2$ (IV; R = Me, Et, Pr^n, or Bu^n). More detailed investigation revealed a more complex reaction behaviour. Thus with the diamide (I; R = Et), the linear dimer, $NR[PhP(:S)NHR]_2$ (III; R = Et), is formed at 180°, the cyclic dimer (IV; R = Et), at 200°, and the dealkylated dimer (IV; R = H) at 225°. The three products were isolated and characterised.

The thermal condensation of the diamide (I; R = Ph) at 265° takes a different course. The product, although its analysis and molecular weight are in agreement with the values expected for the cyclic dimer (IV; R = Ph), yields diphenylphosphinic acid on hydrolytic degradation. We therefore tentatively suggest a novel six-membered-ring structure (V; R = Ph) which is in accord with our experimental findings. A crystallographic examination of this compound is being carried out elsewhere.

The reactions are summarised in the scheme. All compounds have satisfactory analysis and molecular weights. Their ultraviolet, infrared, and ^{1}H n.m.r. spectra are in accord with the structures suggested.

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[2] E. H. M. Ibrahim and R. A. Shaw, unpublished results.

[3] S. Trippett, *J. Chem. Soc.*, 1962, 4731.