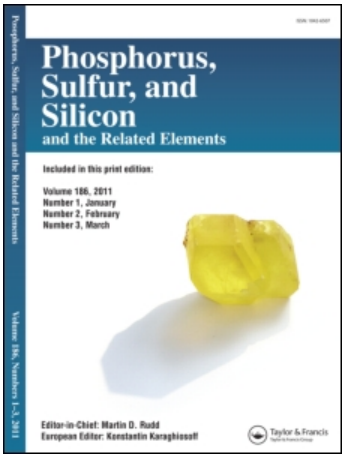

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Reactions of Halides of Tervalent Phosphorus with Imines and -Diimines

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REACTIONS OF HALIDES OF TERVALENT PHOSPHORUS WITH IMINES AND α-DIIMINES

A.M.KIBARDIN, T.V.GRYAZNOVA, P.I.GRYAZNOV, E.Ya.LEVINA, I.A.LITVINOV, V.A.NAUMOV, Yu.B.MIKHAILOV, and A.N.PUDOVIK
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Isobutylidenebutylamine reacts with phosphorus trichloride in the presence of organic bases to give N-butyl-N-isobutenylamidodichloro- or bis(N-butyl-N-isobutenylamido)chlorophosphites depending on the ratio of reagents. Reasons are given in favour of the reaction beginning with the nucleophilic attack of the nitrogen atom of the imine on the electrondeficient phosphorus atom of the chloride. Reactions of ethyldichloro- and diethylchlorophosphites with benzylidenmethylamine produce 2-chloro- and 2-ethyl-2-oxo--1,4,2-diazaphospholanes respectively. Interaction of diethylchlorophosphite with benzylidenmethylamine in the presence of triethyphosphite results in the formation of diethyl(N-methyl-N-α-diethylphosphonobenzylamido)phosphite. As a result of interaction of bis(diethylamino)chlorophosphine with N,N-dibutyl-2,3-butandiimine in the presence of triethylamine new compounds (2-diethylamino-1,3-dibutyl--4,5-dimethyl-1,3,2-diazaphospholane and 4,8-dibutyl-3,7--bis(diethylamino)-[3.3.0]-bicyclooctadiene-1,5) are obtained. The structure of the latter is proved by means of ^{1}H, ^{31}P NMR-spectroscopy, and a complete X-ray analysis. Alkyldichlorophosphines form phosphonium salts of 1,3,2-diazaphospholene structure with α-diimines and 2-chloro-1,3-dicyclohexyl-4-chloro-1,3,2-diazaphospholene resulting from the reaction of N,N-dicyclohexylethylenediimine with PCl_3. In this product the P-Cl bond is unusually long, which is confirmed by X-ray analysis. In the course of the interaction of tervalent phosphorus halides with α,β-unsaturated imines a new reaction has been discovered with the formation of 1,2-dihydro-1,2-azaphosphorines.