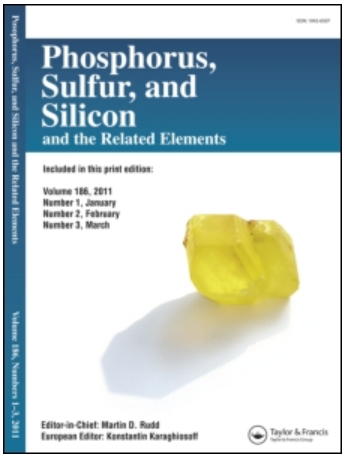

Phosphorus, Sulfur, and Silicon and the Related Elements

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Reactions with Hydrophosphoryl Halides

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In the systems $RPCl_2+H_2O$, $RPCl_2+RCOOH$, $RPCl_2+RPH(O)OH$ and $RPH(O)OH+RCOX$ the formation of hydrophosphoryl halides $RPH(O)X$ (X=Cl,Br,I; R=H,OH,Hal,Alk,AlkO,Ar) was proved by spectral and chemical methods. Hydrophosphoryl halides react with alyphatic ketones R'_2CO yielding phosphinic halides $R[R'_2C(OH)]P(O)X$ (X-ray analysis). In case of aromatic aldehydes and ketones containing electron donor substituentes, the addition products are rearranged into α-halogenalkylphosphinic acids.

$$RPH(O)X + ArCOR' \longrightarrow R[ArC(R')(OH)]P(O)X \longrightarrow R[ArC(R')(X)]P(O)OH$$

Hydrophosphoryl halides readily add to the activated double bond C=C of various unsaturated compounds.

$$RPH(O)Cl + CH_2=CH-COR' \longrightarrow R[R'C(O)CH_2CH_2]P(O)Cl \quad (R'=AlkO,Cl)$$

In the reaction with AcCl α-hydroxyalkylphosphonous acids yield α-hydroxyalkylhydrophosphoryl chlorides which add cyclic ketones to form di-α-hydroxyalkylphosphinic chlorides, for instance:

$$cyclo\text{-}C_6H_{10}(OH)PH(O)OH + AcCl + C_6H_{10}O \longrightarrow [cyclo\text{-}C_6H_{10}(OH)]_2P(O)Cl$$

The substance was recrystallized from acetone (m.p. 103-105°); being hydrolized it is converted into phosphinic acid $[cyclo\text{-}C_6H_{10}(OH)]_2P(O)OH$ (m.p. 199-200°), whose physico-chemical characteristics coincide with those of the specimen obtained by addition of α-hydroxycyclohexylphosphonous acid to cyclohexanone.