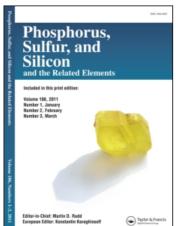
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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Reactions with Hydrophosphoryl Halides

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## Reactions with Hydrophosphoryl Halides

N.A.Kardanov, A.M.Timofeev, G.A.Kvashnina, L.V. Ermanson, N.N. Godovikov and M.I. Kabachnik
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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  $R_2'CO$  yielding phosphinic halides  $R[R_2'C(OH)]P(O)X$  (X-ray analysis). In case of aromatic aldehydes and ketones containing electron donor substituentes, the addition products are rearranged into  $\mathcal{L}$ -halogenalkylphosphinic acids.

RPH(O)X + ArCOR - R[ArC(R')(OH)]P(O)X - R[ArC(R')(X)]P(O)OHHydrophosphoryl halides readily add to the activated double bond C=C of various unsaturated compounds.

RPH(O)Cl + CH<sub>2</sub>=CH-COR' — R[R'C(O)CH<sub>2</sub>CH<sub>2</sub>]P(O)Cl (R'=AlkO,Cl) In the reaction with AcCl  $\mathcal{L}$ -hydroxyalkylphosphonous acids yield  $\mathcal{L}$ -hydroxyalkylhydrophosphoryl chlorides which add cyclic ketones to form di- $\mathcal{L}$ -hydroxyalkylphosphinic chlorides, for instance: cyclo-C<sub>6</sub>H<sub>1O</sub>(OH)PH(O)OH + AcCl +C<sub>6</sub>H<sub>1O</sub>O — [cyclo-C<sub>6</sub>H<sub>1O</sub>(OH)]<sub>2</sub>P(O)Cl The substance was recrystallized from acetone (m.p. 103-105°); being hydrolized it is converted into phosphinic acid [cyclo-C<sub>6</sub>H<sub>1O</sub>(OH)]<sub>2</sub>P(O)OH (m.p. 199-200°), whose physico-chemical characteristics coincide with those of the specimen obtained by addition of  $\mathcal{L}$ -hydroxycyclohexylphosphonous acid to cyclohexanone.