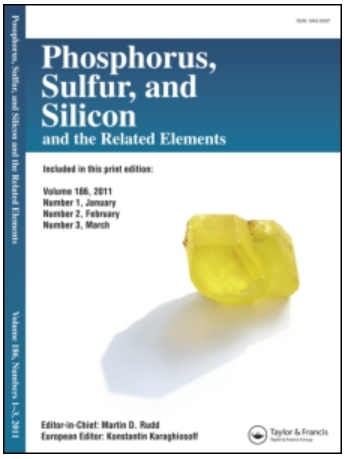

Phosphorus, Sulfur, and Silicon and the Related Elements

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The Active Mixed Anhydrides of Phosphorous Ph-Acids

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THE ACTIVE MIXED ANHYDRIDES OF PHOSPHOROUS PH-ACIDS

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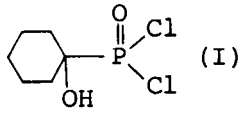
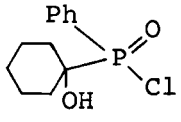
The ^{31}P spectra of H_3PO_3 + Ac_2O and PCl_3 + Ac_2O contain signals which were assigned to the following compounds (δ_P, J_{PH}): H_3PO_3 (8,5; 702), AcO(OH)P(O)H (2,2; 739), $(AcO)_2P(O)H$ (-2,7; 763), $(AcO)_3P$ (131,6); PCl_3 (220,7), $AcOPCl_2$ (194,6), $(AcO)_2PCl$ (167,0), $(AcO)_3P$ (131,5). The active intermediates with -PH(O)Cl groups are formed on treating phosphorous PH-acids with AcCl, and in other reactions[1]. These intermediates are added to aldehydes and ketones resulting in compounds (I), (II) and (III). The compounds of type (II) treated with AcOH transform into compounds of different structure, e.g. into (IV) and (V).


(I)

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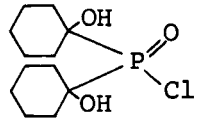
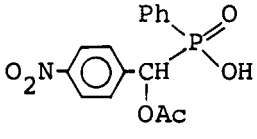

(III)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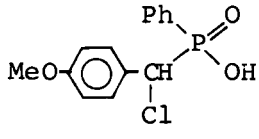
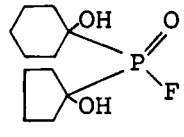

(V)

(VI)

Fluoroanhydride [cyclo-C_6H_{10}(OH)]PH(O)F (δ_P 48,1, J_{PH} 581, J_{PF} 1069) is added to cyclopentanone with the formation of (VI) (m.p. 124-126°C, δ_P 62,6, J_{PF} 1110). The structure of (I)-(V) was proved by X-ray analysis.

1. N.A.Kardanov, A.M.Timofeev, N.N.Godovikov, A.N.Chernega, M.Yu.Antipin, Yu.T.Struchkov, M.I.Kabachnik, Zh.Obsch. Chim. 58, 2038, (1988).