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The Active Mixed Anhydrides of Phosphorous Ph-Acids

N. A. Kardanov^a; A. M. Timofeev^a; G. A. Kvashnina^a; S. A. Trifonova^a; N. N. Godovikov^a; M. I. Kabachnik^a; A. N. Nesmeyanov^a

^a Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Moscow, USSR

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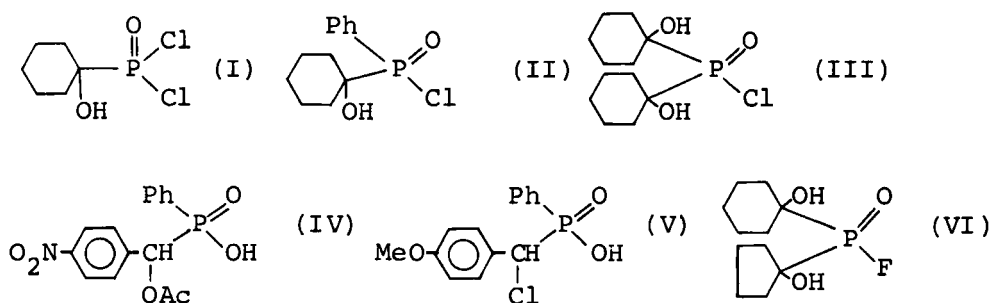
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THE ACTIVE MIXED ANHYDRIDES OF PHOSPHOROUS PH-ACIDS

N.A.KARDANOV, A.M.TIMOFEEV, G.A.KVASHNINA,
 S.A.TRIFONOVA, N.N.GODOVIKOV, and M.I.KABACHNIK
 A.N.Nesmeyanov Institute of Organo-Element Compounds,
 Academy of Sciences of the USSR, Vavilov Str. 28,
 Moscow 117813, USSR

The ^{31}P spectra of $\text{H}_3\text{PO}_3 + \text{Ac}_2\text{O}$ and $\text{PCl}_3 + \text{Ac}_2\text{O}$ contain signals which were assigned to the following compounds (δ_{P} , J_{PH}): H_3PO_3 (8,5; 702), $\text{AcO}(\text{OH})\text{P}(\text{O})\text{H}$ (2,2; 739), $(\text{AcO})_2\text{P}(\text{O})\text{H}$ (-2,7; 763), $(\text{AcO})_3\text{P}$ (131,6); PCl_3 (220,7), AcOPCl_2 (194,6), $(\text{AcO})_2\text{PCl}$ (167,0), $(\text{AcO})_3\text{P}$ (131,5). The active intermediates with $-\text{PH}(\text{O})\text{Cl}$ groups are formed on treating phosphorous PH-acids with AcCl , and in other reactions¹. 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).



Fluoroanhydride [$\text{cyclo-C}_6\text{H}_{10}(\text{OH})$] $\text{PH}(\text{O})\text{F}$ (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).