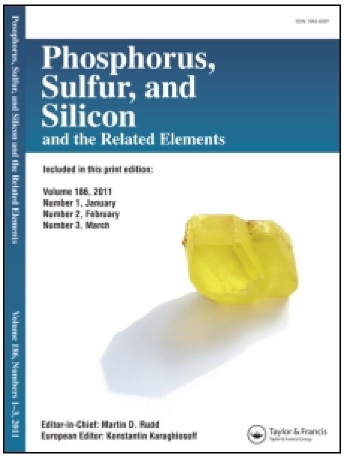

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N-Phospzorylated Esters of Allophanic Acid

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N-PHOSPHORYLATED ESTERS OF ALLOPHANIC ACID

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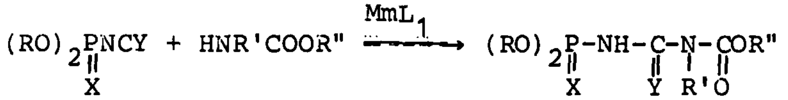
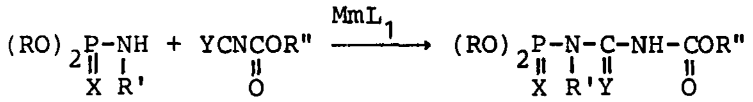
4-Dialkylphosphoryl allophanates have been prepared by reactions of dialkylphosphoryl isocyanates and isothiocyanates with carbamates



$$(RO)_2\underset{\overset{\|}{X}}{P}NCY + HNR'COOR'' \xrightarrow{MmL_1} (RO)_2\underset{\overset{\|}{X}}{P}\text{-NH-}\underset{\overset{\|}{Y}}{C}\text{-}\underset{\overset{|}{R'}}{N}\text{-}\underset{\overset{\|}{O}}{C}OR''$$

and alkoxycarbonyl isocyanates and isothiocyanates with dialkylphosphoramides, both catalyzed by metal salts



$$(RO)_2\underset{\overset{\|}{X}}{P}\text{-}\underset{\overset{|}{R'}}{NH} + YCN\underset{\overset{\|}{O}}{C}OR'' \xrightarrow{MmL_1} (RO)_2\underset{\overset{\|}{X}}{P}\text{-}\underset{\overset{|}{R'}}{N}\text{-}\underset{\overset{\|}{Y}}{C}\text{-NH-}\underset{\overset{\|}{O}}{C}OR''$$

Kinetic measurements of the reaction of methoxycarbonyl isothiocyanates with diisopropylphosphoramide were carried out. The structures of allophanates were confirmed by IR and ^{31}P spectroscopy. Mass spectra of N-phosphorylated allophanates were recorded and the observed fragmentation behavior was compared with that of allophanates, phosphoramides and N-phosphorylated carbamates. One of the pathways of fragmentation observed in mass spectra of allophanates is the skeletal rearrangement with N → O migration. High-resolution measurements were carried out ions discussed in the fragmentation of rearrangement. This pathway was observed for phosphoric carboxylic imides (1), and earlier by us for N-phosphorylcarbamates. The skeletal rearrangement is common in spectra of N-acylamides of phosphorus acid.

(1) V.Mizrahi, T.A.Modro, J. Org. Chem. 47, 3533 (1982).