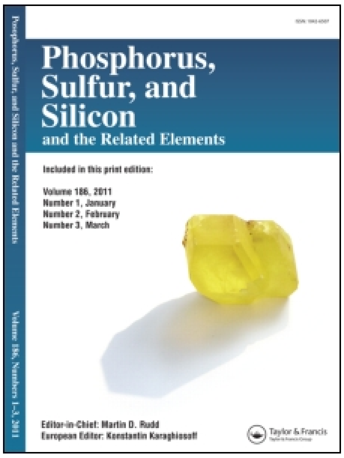

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Studies on the Imide-Amide Rearrangement of Cyclic Phosphorimidates

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Studies on the Imide-Amide Rearrangement of Cyclic Phosphorimidates

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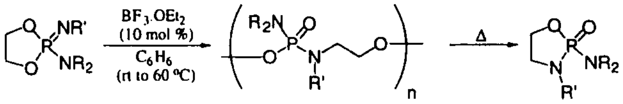
The imide-amide rearrangement of cyclic phosphorimidates **1** leads to the formation of phosphoramidates **3**, either thermally (> 180 °C) or by the action of a Lewis acid (BF_3OEt_2, 60 °C)[1]. In an attempt to develop a synthetic pathway to β-aminoalcohols based on this rearrangement, we have thoroughly studied the influence of the structure of the reactants on the Lewis acid catalysed rearrangement. This study brought some insight into the mechanism of this particular reaction, namely the identification of a new polymeric structure **2**, not yet described, which is converted into **3** by thermolysis[2].
The formation of **2** at rt was followed by ^{31}P NMR. In the case of R' = Ph, the reactivity observed for R_2N was: i-Pr_2N > Pyrrolidine > n-Bu_2N. For R_2 =i-Pr_2, the observed R' group effect was: Bn > 4-NO_2Bn > Ph. No reaction was observed for R' = Ts, n-Oct. In the case of the groups R' = Bn and R_2=i-Pr_2 the Lewis acid effect was also studied: BF_3OEt_2, $BF_3MeO$$t$-Bu, $Sc(OTf)_3$ or $ClTi(O$$i$-$Pr)_3$ > $ZnCl_2$, $MeSnCl_3$ or Me_2SnCl_2.



1 **2** **3**

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