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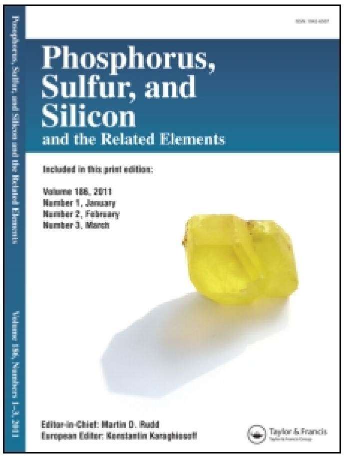

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Nucleophilic and Acid Catalysis in Phosphoramidite Alcoholysis

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NUCLEOPHILIC AND ACID CATALYSIS IN PHOSPHORAMIDITE ALCOHOLYSIS

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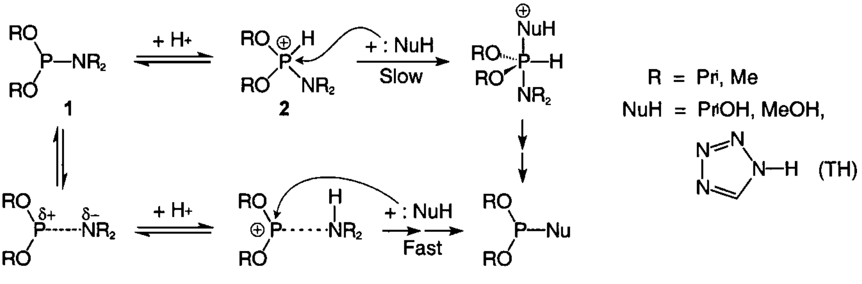
Keywords: ^{31}P NMR; catalysts; oligonucleotides; phosphoramidites; protonation; reaction mechanism

We have studied alcoholysis of phosphoramidites (**1**), a reaction utilized in the automated solid-support synthesis of DNA, in MeCN in presence of various ammonium, pyridinium and azolium salts.[1] The reaction is subject both to acid and nucleophilic catalysis: The salt cation acts as an acid and either the anion or deprotonated cation may act as a nucleophile. The reaction rate depends on the acidity and nucleophilicity of the activator but is independent of the alcohol concentration.

Very strong acids (pK_a(MeCN) <9) protonate the phosphorus atom of **1**. We have characterised the protonated species by ^{31}P NMR and found them to be surprisingly unreactive.[2] This indicates that the fast reactions of **1** catalysed by weak acids can not take place via *P*-protonation. Weak acids can protonate **1** only after P—N bond has been lengthened



SCHEME 1

Address correspondence to Erkki J. Nurminen, Department of Organic Chemistry, Åbo Akademi University, 20500 Åbo, Finland. E-mail: enurmine@abo.fi and the nitrogen become the most basic site of the molecule. Unlike *P*-protonation, *N*-protonation enables the energetically favored dissociative reaction path (lower reaction in Scheme 1).

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