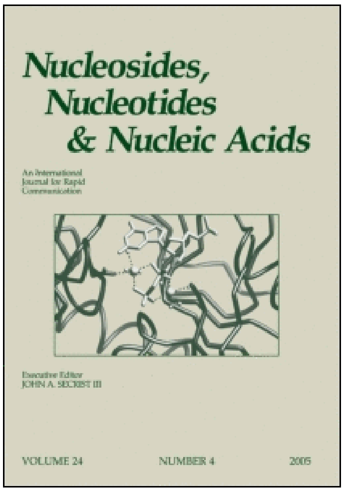

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Silyloxyphosphanes. New Phosphitylating Reagents in Nucleotide Chemistry

W. Dabkowski[a]; J. Michalski[a]; Q. Wang[a]
[a] Polish Academy of Sciences, Centre of Molecular and Macro-molecular Studies, L slashódź, Poland

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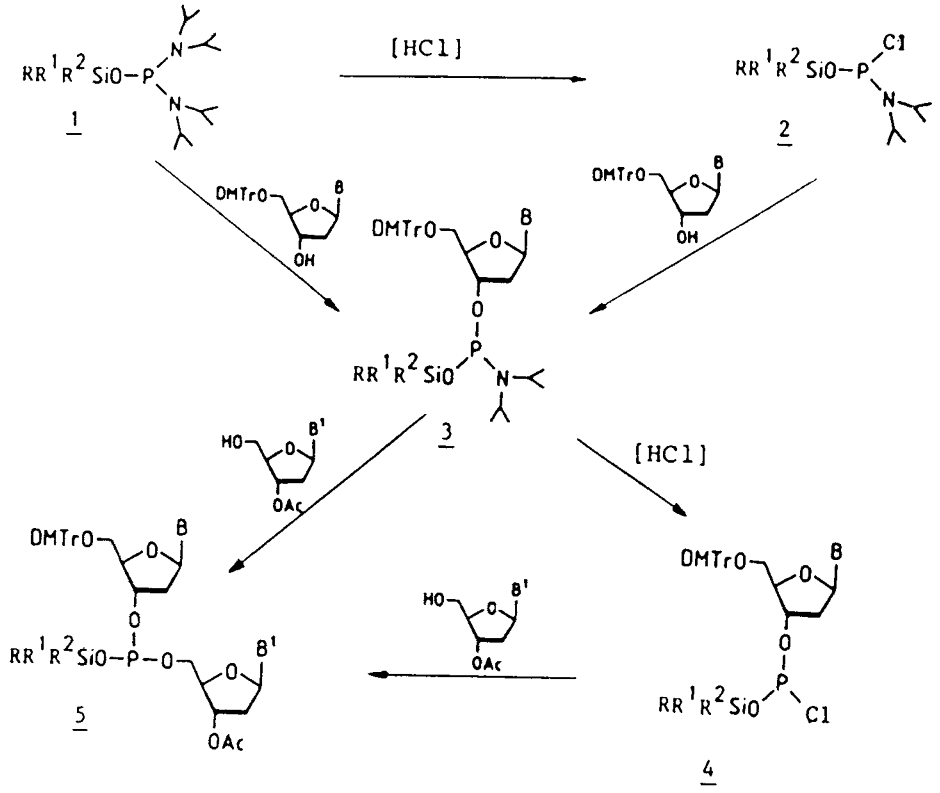
SILYLOXYPHOSPHANES. NEW PHOSPHITYLATING REAGENTS IN NUCLEOTIDE CHEMISTRY

W.Dąbkowski, J.Michalski* and Q.Wang

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland

Letsinger et al. developed a phosphite method of synthesis of oligonucleotides. This method was further improved by Carruthers et al. Our present work is a useful extension of the Letsinger-Carruthers type reagents. Recently, we have been able to demonstrate that bis-(N,N-diisopropylamino)trimethylsilyloxy phosphane exhibit phosphitylating properties in the presence 1-H-tetrazole.[1] Preparation of this reagent and its ability to undergo selective nucleophilic substitution at the tricoordinate phosphorus atom without affecting the silicon center under conditions which are commonly used for the phosphite triester approach has been recently described.[1] In the same paper we reported remarkable chemical properties of dinucleosidetrimethylsiloxyphosphanes. Namely their participation in Michaelis-Arbuzov type reactions under extremely mild conditions and reactions with oxalylazolides and sulfuryl chloride fluoride which are unique for these reagents.

This poster includes our progress in designing new phosphitylating reagents containing trisubstituted siloxy groups. The compounds of the general formula $(Pr^i_2N)_2$ P-OSiR^{1}R^{2}R^3, 1 can be prepared by the similar procedure as has been described before.[1] The reaction with aniline hydrochloride or hydrogen chloride generated in situ leads to chlorophosphite 2. This reagent allows fully selective phosphitylation of 3'-deoxynucleosides leading to nucleoside trisubstituted siloxyphosphane 3. The siloxyphosphane 3 when allowed to reacts with hydrogen chloride donors gives the chlorophosphane 4. The latter reacts smoothly with 5'-nucleoside to give dinucleoside siloxyphosphites 5 in excellent yield. Reactions employed in this approach are fast and highly selective. New intermediates described can serve as the starting materials in the synthesis of a wide variety of modified nucleotides.



1. W.Dąbkowski, J.Michalski, Q.Wang, Angew.Chem., Int.Ed., 1990, 5, 522-523, and references cited therein.