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Dinucleoside (5' → 3')-O,S-Phosphorodithioates - New Class of Dinucleotide Analogues

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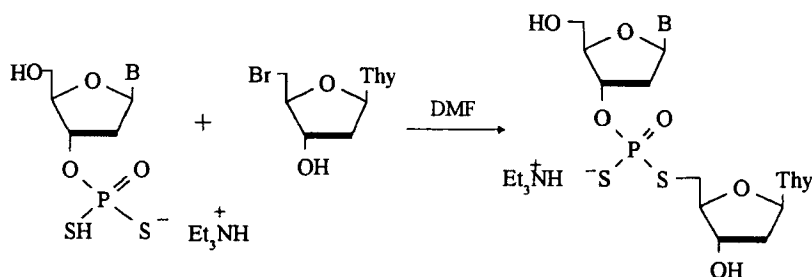
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DINUCLEOSIDE (5'→3')-O,S-PHOSPHORODITHIOATES- NEW CLASS OF DINUCLEOTIDE ANALOGUES

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Nucleoside 3'-O- and 5'-O-phosphorodithioates have been recently described by Caruthers *et al.*¹ as a new type of nucleotide analogues. These compounds have also been obtained in our Laboratory by one-pot dithiaphospholane approach.² We now report on the transformation of some of these derivatives into new class of dinucleotide analogues. We have found that nucleoside 3'-O-phosphorodithioates (1) react in DMF solution with 5'-bromo-5'-deoxythymidine to give in high yield corresponding dinucleoside (5'→3')-O,S-phosphorodithioates (2) - first examples of a new class of dinucleotide analogues possessing the internucleotide phosphorothioate linkage with one of the sulfur atoms in a 3'-bridging position.



1a, B=Thy

1b, B=Cyt

2a, B=Thy, δ ³¹P NMR =72.9, 73.6ppm

2b, B=Cyt, δ ³¹P NMR =72.8, 73.5ppm

The products **2a,b** were isolated by ion exchange chromatography as a mixture of diastereomers by virtue of asymmetry of internucleotide phosphorus as evidenced by ³¹P NMR and HPLC. Their structure was confirmed by characteristic ³¹P NMR chemical shift and by LSIMS mass spectrometry.

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