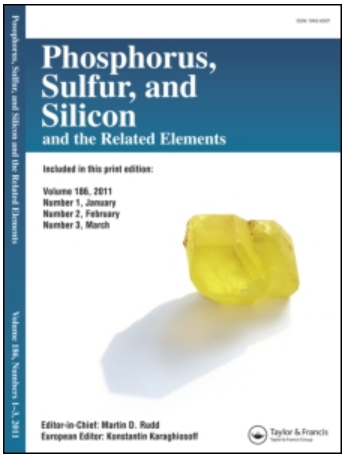

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Deoxyribonucleoside Cyclic 3',5'-Phosphorofluondates

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DEOXYRIBONUCLEOSIDE CYCLIC 3',5'-PHOSPHOROFLUORIDATES

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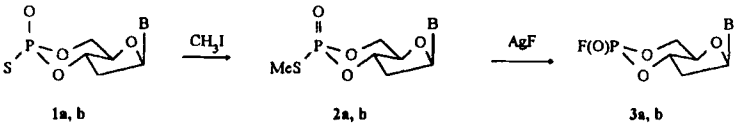
The synthesis of nucleoside cyclic 3',5'-phosphorofluoridates, so far not described compounds in the chemical literature, have been performed. As a key substrate we used 2'-deoxyribonucleoside cyclic 3',5'-phosphorothioates (**1**) which have been obtained in this Laboratory several years ago.[1]

Alkylation of the triethylammonium salt of **1** with methyl iodide and subsequent treatment of 2'-deoxyribonucleoside cyclic 3',5'-(S-methyl)phosphorothioates (**2**) with aqueous silver fluoride[2] (Scheme 1) gave **3**.



The reaction progress was monitoring by means of ^{31}P nmr. If pure [Sp]-**1a** was used as the substrate, crude **3a** consisted of the mixture of diastereoisomers absorbing at -7.3 ppm and -9.0 ppm (CD_3CN) with $^1J_{P-F}$ 923 and 948 Hz, respectively in the ratio 9:1. Pure [Rp]-**1a** under analogues condition gave as the product **3a**; the ratio of diastereomer absorbing at -7.3 ppm and -9.0 ppm equal 2:1. Treatment of this mixture with concentrated aq. NH_3 caused epimerization process leading exclusively to **3a** resonating at -7.3 ppm ($^1J_{P-F}$ 923 Hz). When we performed the conversion of phosphorothioate into phosphorofluoridate starting from diastereomeric mixture of deoxycytidine cyclic 3',5'-phosphorothioates (**1b**, Sp:Rp=2:1, Scheme 1) exclusively one diastereomer of **3b** (δ_{31P} -7.9 ppm, $^1J_{P-F}$ 950 Hz) was obtained.

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