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### 5-Substituted 2-(Pyrimidin-2-yl)-Ethanol as New Phosphate Protecting Groups

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5-SUBSTITUTED 2-(PYRIMIDIN-2-YL)-ETHANOLS AS NEW  
PHOSPHATE PROTECTING GROUPS

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We synthesized some  $\beta$ -H acidic 2-(pyrimidin-2-yl)-ethanols as protecting groups for the phosphotriester method and studied the kinetics of their removal by HPLC.

The condensation of  $\alpha$ -R-substituted  $\beta$ -dimethylamino-acroleins (1) with hydroxypropioamide hydrochloride (2) gives the 5-substituted 2-(pyrimidin-2-yl)-ethanols 2a-d (3). Their reaction with 5'-O-methoxytritylthymidine and 2,5-dichlorophenylphosphorobistriazolidine in dry pyridine leads to the corresponding triesters 3a-d (4).

The phosphotriesters were detritylated in good yields using *p*-toluenesulfonic acid (1 % in chloroform/methanol 4:1), and the 2,5-dichlorophenyl group was cleaved to the corresponding phosphodiester using *p*-nitrobenzaldehyde (5).

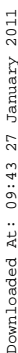
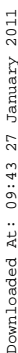
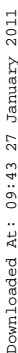
The removal of the pyrimidinylethyl groups was followed by reversed phase HPLC in relation to the corresponding *p*-NPE-triester 3e (4). As a result we found that the cleavage either with DBU/DBN or triethylamine takes place via  $\beta$ -elimination.

The removal with 0.5 M DBU (10-fold molar excess) in dry pyridine or acetonitrile shows the usefulness of the new heterocyclic protecting groups: the cleavage occurs in general faster than does in 3e.

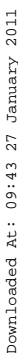
0.5 M DBN shows in principle the same sequence, but the rate is about a factor of 2 lower than with DBU.

Subsequently we studied the behaviour of the new protecting groups with triethylamine (phosphotriester/ $\text{NEt}_3$  1:163). All five triesters are cleaved with anhydrous triethylamine/pyridine, the  $\tau$ -values range from two hours (3b) up to 35 hours (3c).

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