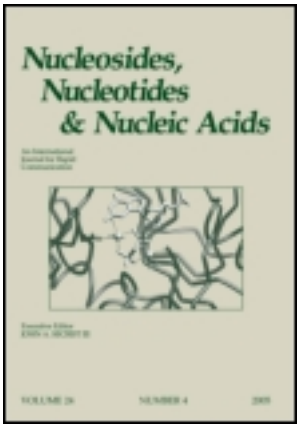


Nucleosides and Nucleotides
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lncn19

A Novel Route for the Synthesis of Fluorodeoxy Sugars and Nucleosides

Igor A. Mikhailopulo [a] , Grigorii G. Sivets [a] & Natalia B. Khripach [a]
[a] Institute of Bioorganic Chemistry, National Academy of Sciences , Acad. Kuprevicha 5, 220141, Minsk, Belarus
Published online: 04 Oct 2006.

To cite this article: Igor A. Mikhailopulo , Grigorii G. Sivets & Natalia B. Khripach (1999) A Novel Route for the Synthesis of Fluorodeoxy Sugars and Nucleosides, Nucleosides and Nucleotides, 18:4-5, 689-690, DOI: 10.1080/15257779908041542

To link to this article: http://dx.doi.org/10.1080/15257779908041542

NUCLEOSIDES & NUCLEOTIDES, 18(4&5), 689–690 (1999)

A NOVEL ROUTE FOR THE SYNTHESIS OF FLUORODEOXY SUGARS AND NUCLEOSIDES

Igor A. Mikhailopulo*, Grigorii G. Sivets and Natalia B. Khripach.

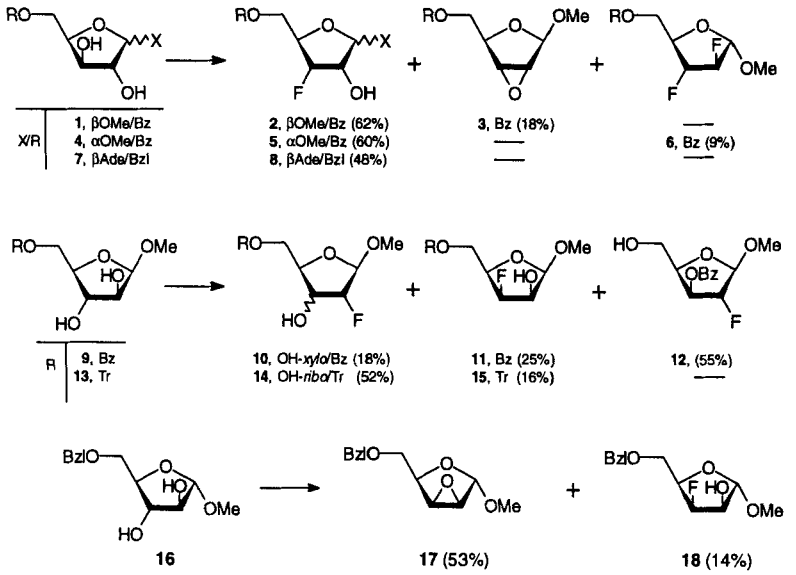
Institute of Bioorganic Chemistry, National Academy of Sciences, 220141 Minsk, Acad. Kuprevicha 5, Belarus

ABSTRACT: Ring-fluorination of α- and β-D-pentofuranosides containing free secondary hydroxyl groups by (diethylamino)sulfur trifluoride (DAST) was studied.

Recently, we have described a new alternative for the preparation of 2,3-*cis* fluorodeoxy pentofuranosides using the reaction of (diethylamino)sulfur trifluoride (DAST) with methyl 5-O-benzyl-β-D-arabinofuranoside and its *xylo*-isomer[1]. This study was continued and expanded, and especially focused on the influence of the configuration at the anomeric center and the nature of the 5-O-blocking group on the course of the transformation.

Treatment of methyl 5-O-benzoyl-β-D-xylofuranoside (**1**) with DAST in a molar ratio of 1:6 in anhydrous dichloromethane at room temperature for 19 h, followed by silica gel column chromatography, afforded the β-riboside **2** and the *ribo*-epoxide **3** in 62 and 18%, respectively. Under similar reaction conditions with the α-anomer **4** as starting material, the reaction was complete within 4 h at room temperature and the α-riboside **5** and the difluoride **6** were isolated by silica gel column chromatography[1] in 60 and 9% yield, respectively. Treatment of the β-xyloside **7** with DAST[1] gave, after chromatographic purification, the riboside **8** as the principal product (48%). These results point to the fact that the C(3)-O-SF_2NEt_2 derivatives are initially formed in the case of the xylosides. The distinctive feature of the reaction of DAST with the β-

arabinoside **9** (r.t., 5 h) consists in the formation of a 5,3-benzoxonium ion on one of the consecutive transformations which finally give rise to the inversion of the configuration at C(3) affording the xylosides **10** (18%) and **12** (55%); the lyxoside **11** was also isolated from the reaction mixture in a yield of 25%. In the presence of a non-participating 5-O-trityl group, compounds **14** and **15** were isolated in 52 and 16% yield, respectively, from the reaction products of **13** with DAST (r.t., 18 h). It may be thus reasonable to conclude that in the case of the β-arabinosides **9** and **13** the principal route of the reaction is the formation of the intermediate C(2)-O-SF_2NEt_2. Unlike **13**, the α-arabinoside **16** was converted (CH_2Cl_2/Py 1:1, r.t., 5 h) to the *lyxo*-epoxide **17** (53%) and the lyxoside **18** (14%) implying an intermediary formation of the C(3)-O-SF_2NEt_2 derivative.



In conclusion, we have demonstrated that the preparation of some fluorinated carbohydrates may be achieved in a good overall yield starting from the commercially available sugars. This approach provides a useful alternative to the previously described methods.

Acknowledgment: Financial support from the Alexander von Humboldt-Foundation (Bonn/Bad-Godesberg, Germany) is gratefully acknowledged.

REFERENCE

1 Mikhailopulo, I.A.; Sivets, G.G. *SynLett* **1996** (1), 173-174.