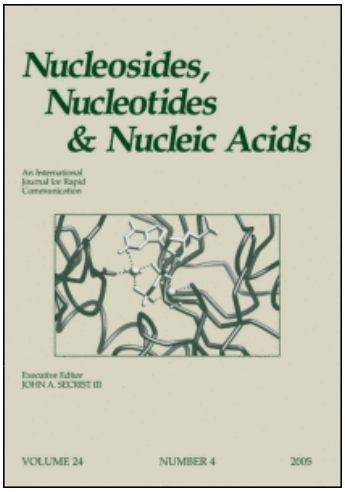

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Nucelosides/Tides Abstracts

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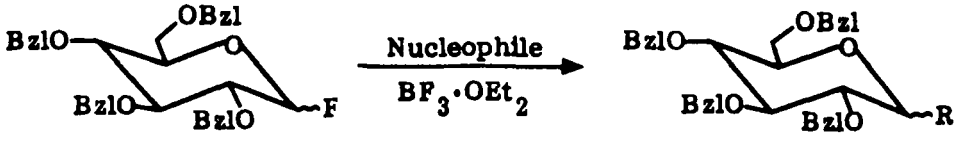
NUCLEOSIDES & NUCLEOTIDES, 5(2), 229-232 (1986)

NUCLEOSIDES/TIDES ABSTRACTS

Compiled by Dr. Marshall W. Logue, Michigan Technological University

Glycosyl Fluorides: Reagents for C-Glycoside Synthesis



Nucleophile	R	% Yield
$Me_3SiCH_2CH=CH_2$	CH_2-CH=CH_2	95
Me_3SiCN	CN	90
Me_3SiCH_2CN	CH_2CN	85
$PhC(OSiMe_3)=CH_2$	CH_2COPh	95
$CH_2(CH_2)_2CH=C\text{-}OSiMe_3$	$CH\text{-}(CH_2)_3\text{-}C=O$	89

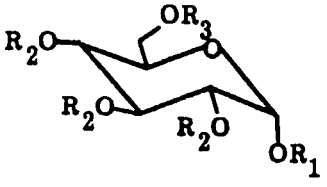
High yield C-glycosidation of glycosyl fluorides occurs readily at 0°C in dichloromethane in the presence of boron trifluoride etherate. In addition to the reactions listed above for the glucosyl fluoride, hepta-O-benzyl-α-β-D-cellibiosyl fluoride reacts with allyltrimethylsilane and 1-(trimethylsilyloxy)-cyclopentene to produce the corresponding glycosides in 59 and 90% yields, respectively. Both the glucosyl and cellibiosyl fluorides react with magnesium bromide etherate at 25°C to give the glycosyl bromides in 90% yield (α:β>20:1).

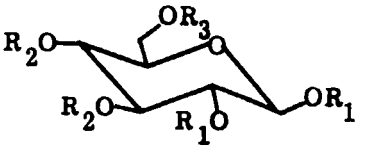
 0732-8311/86/0502-0229$3.50/0

The glucosyl fluoride can also be reduced to the parent tetrahydropyran in 90% yield by aluminum hydride [Very Limited Experimental].

K. C. Nicolaou, R. E. Dolle, A. Chauholowski, and J. L. Randall, J. Chem. Soc., Chem. Commun., 1153-1154 (1984).

Selective Iodination of Monosaccharides with In Situ Iodotrimethylsilane





1a, R_1 = H, R_2 = R_3 = Ac

1b, R_1 = Me, R_2 = R_3 = Ac

1c, R_1 = Me, R_2 = Ac, R_3 = Tr

1d, R_1 = Me, R_2 = Ac, R_3 = H

2a, R_1 = R_2 = R_3 = Ac

2b, R_1 = Bz, R_2 = R_3 = Ac

2c, R_1 = R_2 = Ac, R_3 = H

2d, R_1 = R_2 = Ac, R_3 = Tr

The reagent system of chlorotrimethylsilane/sodium iodide/acetonitrile is very selective towards cleavage of O-acyl and O-alkyl derivatives of monosaccharides, with and without concomitent iodination. In general, free anomeric hydroxyls and their acetates or benzoates are readily converted into the corresponding anomeric iodides, whereas the anomeric O-methyl function is much less reactive. For other primary and secondary hydroxyl functions, their acetates and benzoates are inert, but their ether derivatives are readily cleaved. For the anomeric position the order of reactivity is OAc > OBz ≅ OH ≫OMe, whereas at other positions the order is OTr > OBzl(prim) > OMe(prim) > OBzl(sec) ≫ OBzl(anom.) ≅ OMe(anom.). Mild conditions (30 min, 23°C) allow for simple cleavage, e.g. **1e** to **1d**. Stronger conditions (1-4 h, 60-80°C) allow cleavage with iodination, e.g., **1a**, **1b**, **2a**, and **2b** are converted into the corresponding α-glucosyl iodide; **1c**, **1d**, and **1e** are converted into the

corresponding 6-deoxy-6-iodo derivative; and **2c** and **2d** are converted into the corresponding 6-deoxy-6-iodo-α-D-glucosyl iodide. In addition, 1,2,4,6-tetra-O-acetyl-3-O-benzyl-β-D-glucopyranose can be selectively converted into its corresponding α-glucosyl iodide [Complete Experimental].

A. Klemer and M. Bieber, Justus Liebigs Ann. Chem., 1052-1055 (1984).

Rapid Deprotection of Oligonucleotides Formed by the Phosphotriester Method

An equimolar solution of 1,1,3,3-tetramethylguanidine and either p-nitrobenzaldoxime or pyridine-2-carboxaldoxime at 70°C rapidly removes both base and phosphate protecting groups and cleaves the 3'-succinyl groups binding the oligonucleotide to the solid support. This method is simpler and faster than the oximate method and can easily be incorporated into the cycle of an automated synthesizer. There is no evidence of base modification by the reagents after 24 hours [Complete Experimental].

T. P. Patel, M. A. Chauncey, T. A. Millican, C. C. Bose, and M. A. W. Eaton, Nucleic Acids Res., **12**, 6853-6859 (1984).

Tetraphenylphosphonium Hydrogendifluoride as a Source of Fluoride Ion

The title compound is a thermally stable source of fluoride ion and is readily soluble in polar aprotic solvents such as acetonitrile and dimethyl sulfoxide (also soluble in halogenated aliphatic solvents such as chloroform). The reagent is readily prepared from tetraphenylphosphonium bromide via ion exchange and dehydration of the initially formed monohydrate. Unlike other fluoride ion sources it is easily dried and once dried, only picks up limited

amounts of water from the atmosphere over long periods of exposure. The following reactions illustrate its utility:

Reactant	Product	Solvent	T(°C)/ Time(h)	% Yield
$PhCH_2Br$	$PhCH_2F$	MeCN	52/2.5	100
$2,4\text{-}(NO_2)_2C_6H_3Cl$	$2,4\text{-}(NO_2)_2C_6H_3F$	MeCN	80/2	100
$PhCH_2Br$	$PhCH_2OMe$	MeOH	52/4	100
PhCH=CHCOPh, $EtNO_2$	$MeCH(NO_2)\text{-}CH(Ph)CH_2\text{-}$ COPh	MeCN	25/1	100

Although the monohydrate reacts similarly to the anhydrous salt, the rates of reaction are drastically reduced [Partial Experimental].

S. J. Brown and J. H. Clark, J. Chem. Soc., Chem. Commun., 672-673 (1985).

Pyridinium Poly(Hydrogen Fluoride): Reagent for Glycosyl Fluoride Synthesis

Pyridinium poly(hydrogen fluoride) efficiently converts free, anomeric hydroxyl groups of partially protected monosaccharides into fluorides. The reagent works well with both furanoses and pyranoses in which the other hydroxyls are protected with benzoyl, acetyl, or benzyl functions. Isopropylidene derivatized sugars can serve as substrates, but yields of glycosyl fluorides are low. Ribo- and arabinofuranoses give anomeric mixtures of fluorides, whereas gluco-, manno-, and galactopyranoses give the thermodynamically more stable *α*-glycosyl fluorides regardless of either a cis or trans relationship with a participating group at C-2. The procedure requires simply shaking pyridinium poly(hydrogen fluoride) with the sugar in either anhydrous acetone or dichloromethane at room temperature for 2-12 hours [Partial Experimental].

W. A. Szarek, G. Grynkiewicz, B. Doboszewski, and G. W. Hay, Chem. Lett., 1751-1754 (1984).
