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Review

Methods of synthesis of glycosyl fluorides

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Abstract

In recent years glycosyl fluorides have been utilized as versatile sugar donors in the synthesis of natural products and carbohydrates. This paper provides an update on the advances made in the preparation of glycosyl fluorides during the last decade (1988–1998).

Keywords: Fluorination for sugar anomer position; Fluorination reagents; Fluorination procedures

Contents

1. Introduction

In recent years, glycosyl fluorides have been utilized as versatile sugar donors in the synthesis of natural products and carbohydrates. Glycosyl fluorides have also drawn much attention in biochemistry due to their potential as enzyme inhibitors [1], useful biological probes and substrates for biochemical glycosidation. Usually glycosyl bromides, chlorides and sometimes iodides have been used as glycosyl donors acting as electrophiles in the presence of various activators. Since 1981 glycosyl fluorides have been utilized for effective glycosylation reactions [2] because of their enhanced stability, ease of handling and higher stereoselectivity compared with other

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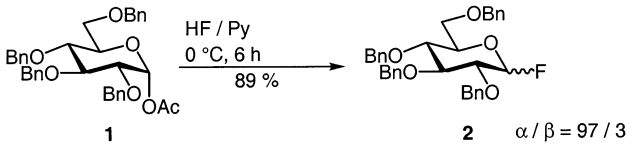
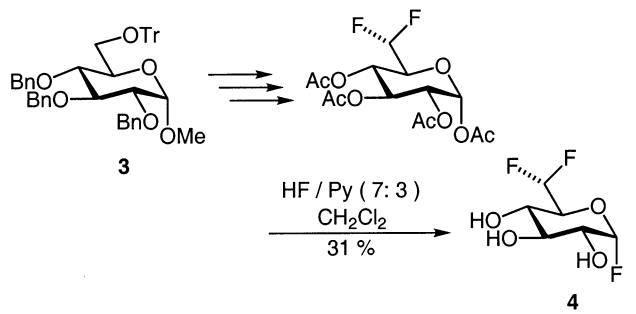


Scheme 1.



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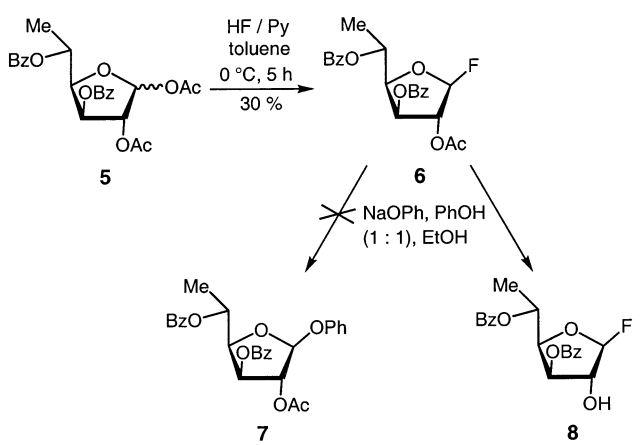

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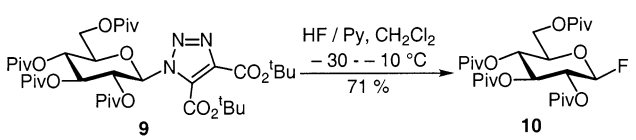

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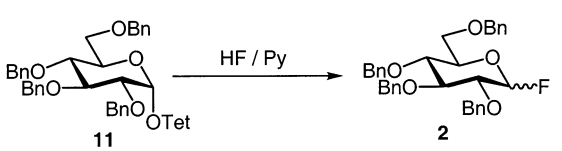


Scheme 5.

glycosyl halides. Some excellent reviews on fluorinated sugars have covered the literature up to 1988 [3–8]. This review article provides an update on the advances made in the preparation of glycosyl fluorides mainly during the last decade (1988–1998) complementary to our recent review on the subject [9].

2. Preparation of glycosyl fluorides

Many studies for preparing the glycosyl fluorides have led to the development of useful fluorination reagents. In this section, synthesis of glycosyl fluorides using several reagents are discussed.

2.1 Hydrogen fluoride.

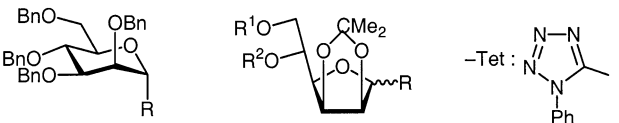
Hydrogen fluoride has been applied to fluorination of sugars. Both 1-hydroxy and 1-O-acetylated sugars have been converted into the corresponding glycosyl fluorides using a 50–70% hydrogen fluoride–pyridine mixture [pyridinium poly(hydrogen fluoride)] (HF–Py) [10]. Compared with the 1-hydroxy sugars, the 1-O-acetylated sugars effectively underwent the fluorination. 1-*O*-Acetyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**1**) afforded the glycosyl fluoride in 89% yield with α-selectivity (Scheme 1). Under a more acidic HF system such as HF itself, HF–nitromethane, or HF–pyridine, when performed at a temperature above 0 °C, the thermodynamically more favored α-glycopyranosyl fluorides (D-series) were formed due to the strong anomeric effect of the fluorine atom, while at low temperature (− 30 ∼ − 75 °C) in the HF system, the kinetically favored β-fluorides were obtained. However, this finding was not applicable to the furanosyl fluorides because of their weaker anomeric effect.

6-Deoxy-6,6-difluoro-α-D-glucopyranosyl fluoride (**4**), an enzyme inhibitor, was synthesized from methyl 2,3,4-tri-*O*-benzyl-6-*O*-trityl-α-D-glucopyranoside (**3**) [11] (Scheme 2).

In a similar fashion, 2-*O*-acetyl-3,5-*O*-dibenzoyl-6-deoxy-β-D-*gluco*-1,4-hexofuranosyl fluoride (**6**) was prepared from **5** [12]. Treatment of **6** with 1 equiv each of PhONa and PhOH gave the deacetylated compound **8** without the expected phenyl glycoside **7** (Scheme 3).

N-Glycosyl triazole derivatives [13,14] such as **9** devised as a new glycosyl donor can be used to prepare the corresponding glycosyl fluorides (Scheme 4).

Table 1
Reaction of OTet glycosides with HF–pyridine



12 R = OTet **14** R = OTet ; R^1, R^2 = Me_2C
13 R = F **15** R = F ; R^1, R^2 = Me_2C
16 R = F ; R^1 = H ; R^2 = H

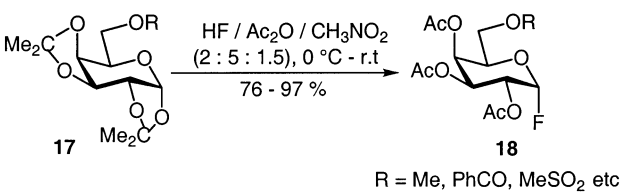
Entry	OTet glycoside (α-D/β-D)	Equiv	Temp. (°C)	Time (min)	Glycosyl fluoride (α-D/β-D)	Yield (%)
1	**11** (100/0)	160	0	30	**2** (90/10)	95
2	**11** (82/18)	5	0	10	**2** (88/12)	89
3	**11** (63/37)	5	0	10	**2** (57/43)	90
4	**12** (100/0)	10	0	10	**13** (100/0)	76
5	**14** (100/0)	5	0	3	**15** (100/0)	12
					16 (100/0)	12
6	**14** (100/0)	5	−20	10	**15** (92/8)	72
					16 (100/0)	10

Treatment of the 1-glycosyl-1,2,3-triazole derivative **9**, derived from the corresponding azide, with the HF–Py complex furnished the corresponding β-glycosyl fluoride **10** at low temperature. However, generally, the ratio of the α and β anomers of the resultant fluoride depends on the protecting group in the 2-position and on the reaction conditions.

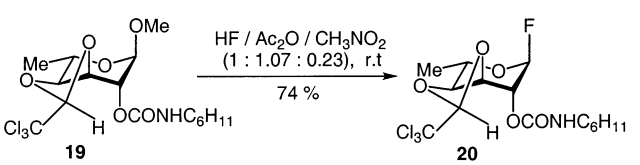
[1-Phenyl-1*H*-tetrazol-5-yl (Tet)]glycosides (**11**, **12**, and **14**) were used to generate the corresponding fluoride with hydrogen fluoride–pyridine [15] (Scheme 5, Table 1).

O-Perbenzylated D-glucopyranoside **11** and D-mannopyranoside **12** could be converted into the corresponding fluorides **2** and **13** in good yields, respectively. The starting OTet configuration seems indifferent for the ratio of fluoride prepared, but it is dependent on the reaction conditions. The reaction of the α-D-mannofuranoside **14** bearing acid-sensitive groups with 5 equiv of HF–Py at 0 °C for 3 min gave the corresponding α-fluoride **15** (46%) in addition to the diol **16** (12%). When the reaction was performed at lower temperature to suppress the acetal cleavage, the yield of **15** increased to 72% with slight accompaniment of the β-fluoride.

A simultaneous fluorination/acylation of sugars was achieved by treatment of acetal-protected monosaccharides (including all types of *O*-, *N*- and *S*-glycosides) using an HF–carboxylic acid–anhydride–CH_3NO_2 system [16–18]. All of the free nonglycosidic hydroxy groups and those protected by acid-sensitive acetal functions are acylated, whereas the other usual protecting groups are not attacked. Undesired ring expansions of furanose rings or contraction of pyranoses are completely suppressed. Thus, 2,3,5,6-tetra-*O*-acetyl-D-glucofuranosyl fluorides were prepared in high yield from methyl D-glucofuranoside or 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose with HF–Ac_2O–CH_3NO_2 [18]. 6-O-Substituted 2,3,4-tri-*O*-acetyl-α-D-galactopyranosyl fluorides **18** can be prepared from 6-O-substituted 1,2:3,4-di-*O*-isopropylidene-D-galacto pyranoses **17** [16] (Scheme 6). When pivaloyl anhydride was chosen as the co-agent, the corresponding tri-*O*-pivaloyl-protected glycosyl fluorides were obtained. When



Scheme 6.



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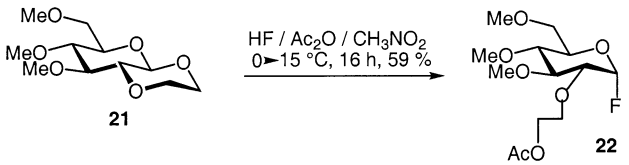
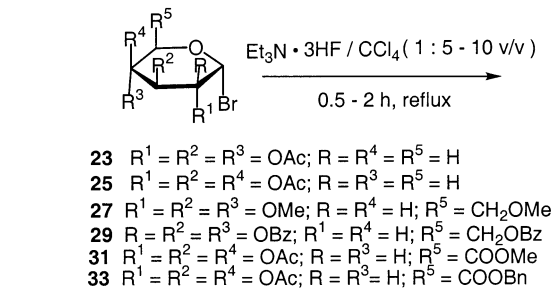
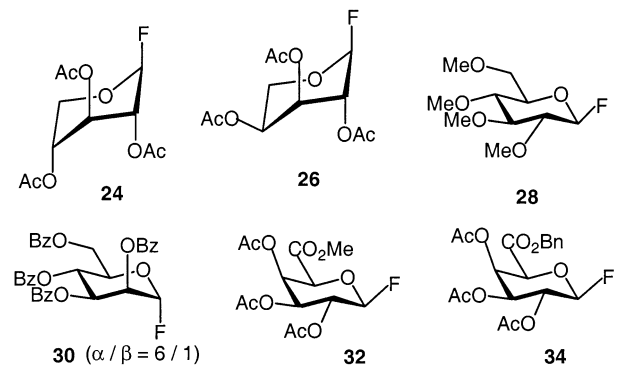
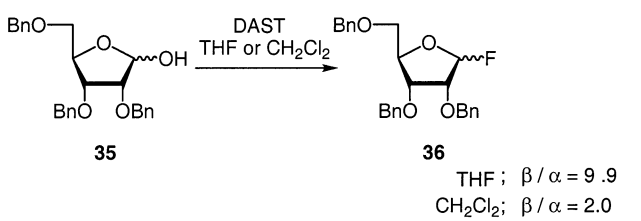


Scheme 8.

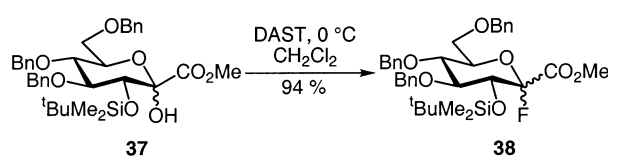




Scheme 9.



Scheme 10.



Scheme 11.

the L-*altro* derivative **19** was treated with HF–Ac_2O–CH_3NO_2, the corresponding α-fluoride **20** was obtained (74%) without removal of the protecting groups [17] (Scheme 7).

The reagent system (HF–Ac_2O–CH_3NO_2) is also suitable to cleave the very stable decaline-type glycosides such as **21**. Thus, 1,2-*O*-ethanediyl-β-D-glucopyranoside **21** was converted into 2-*O*-(acetoxyethyl)-3,4,6-tri-*O*-methyl-α-D-glucopyranosyl fluoride (**22**) [19] (Scheme 8).

A weaker acidic HF system, Et_3N–3 HF, is suitable for preparation of kinetically favored β-glycosyl fluorides [20]. Thus, the pyranosyl fluorides of D-xylose, L-arabinose, D-glucose, D-mannose, and L-rhamnose derivatives as well as of D-galacturonic acid esters were prepared from the corresponding glycosyl bromides using this reagent by bromine–fluorine exchange (Scheme 9).

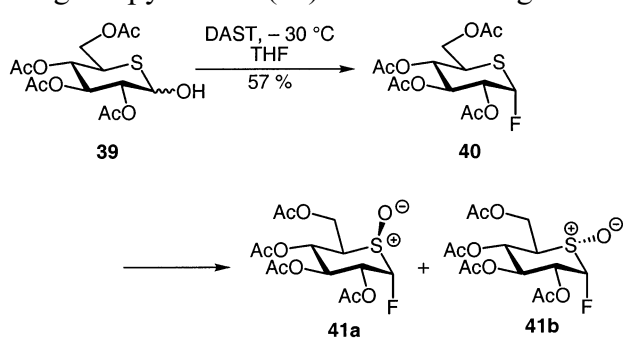
2.2. Diethylaminosulfur trifluoride

Since diethylaminosulfur trifluoride (DAST) was found to be an excellent reagent for replacement of free hydroxyl groups with fluorine [14], it has been utilized widely as the most convenient reagent [8,22]. First application for the anomeric hydroxyl groups was reported in 1985 [3,21].

The α/β ratio of the resulting glycosyl fluoride depends on the species of solvent. When 2,3,5-tri-*O*-benzyl-D-ribose (**35**) was treated with DAST in THF, the β/α ratio of **36** was 9.9, which was changed to β/α = 2.0 when CH_2Cl_2 was used [23] (Scheme 10).

Treatment of hemiacetal **37** with DAST gave a diastereomeric mixture of fluorides **38** in 94% yield [24] (Scheme 11). Coupling of **38** with methanol under the standard conditions, however, failed to give products, only recovering **38**.

The treatment of 2,3,4,6-tetra-*O*-acetyl-5-thioglucopyranose (**39**) with DAST gave the



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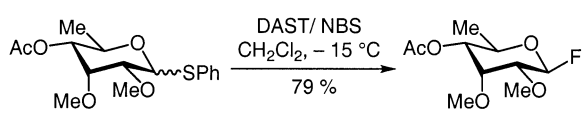
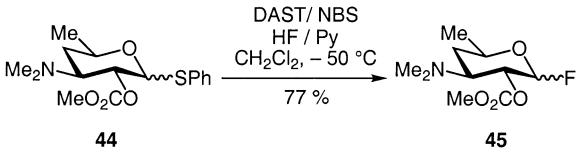


Scheme 13.

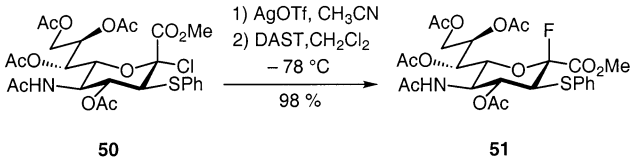


Scheme 14.

glycosyl fluoride **40** in 57% yield. The MCPBA oxidation of **40** afforded the corresponding sulfoxides with axial (**41a**) and equatorial (**41b**) isomers [25] (Scheme 12).

The conversion of thioglycosides into glycosyl fluorides can be demonstrated by the concomitant use of DAST and NBS (*N*-bromosuccinimide) [26]. Thus, phenyl thioglycoside **42** afforded the fluoride **43** in 79% yield [27] (Scheme 13).

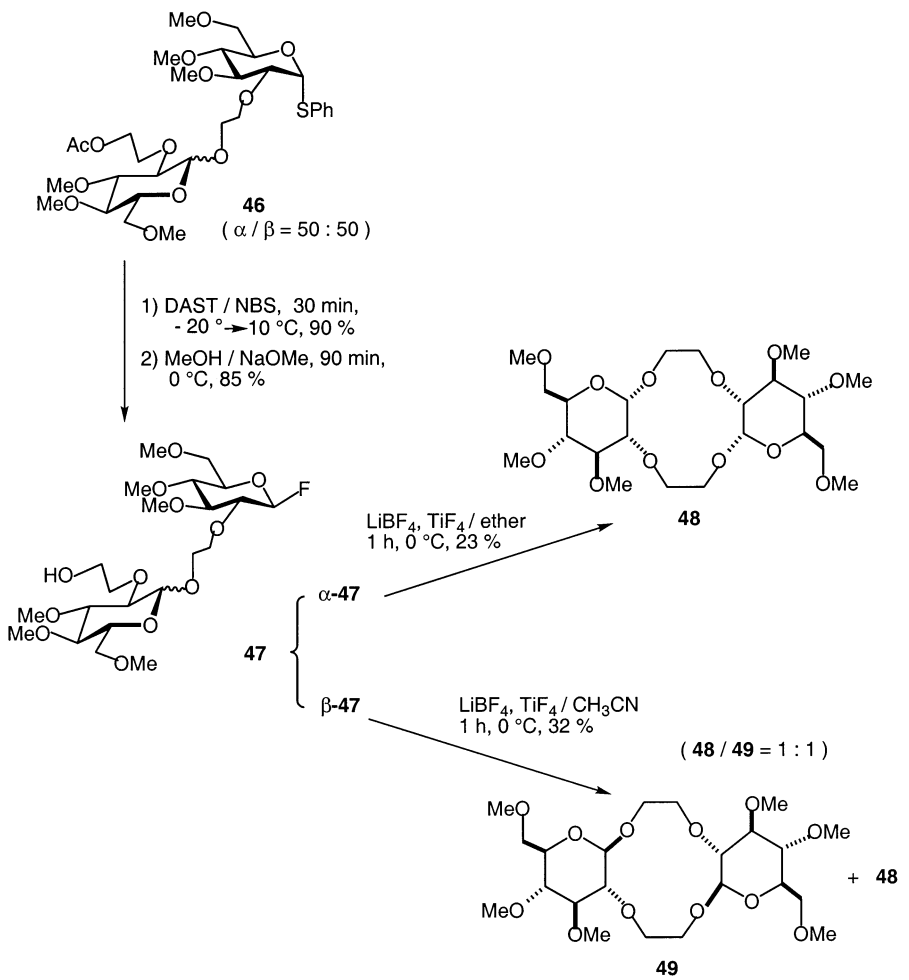
However, conversion of thioglycoside **44** into the fluoride **45** under the same conditions did not occur [28]. It was considered that the competitive attack of NBS to both the PhS and Me_2N groups was the reason for the failure. In order to make a selective attack on the PhS group, HF–Py was added as a co-activator under the standard conditions (regioselective protonation of Me_2N group) at a lower temperature, whereupon **45** was obtained in 77% yield (Scheme 14).



Scheme 16.

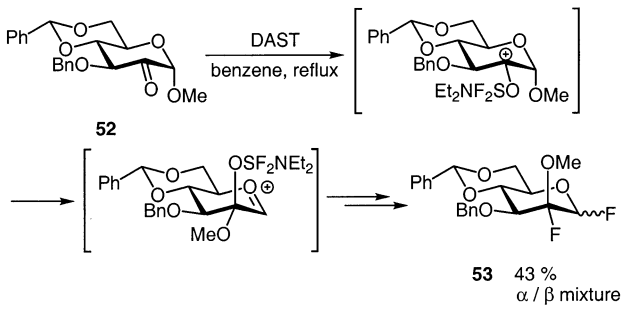
Miethchen and co-workers also used the combination of DAST and NBS to prepare β-glycosyl fluoride **47** from α-thioglycoside **46** [18]. Compound **47** was used to prepare bis(D-glucopyranosido-12-crown-4) derivatives **48** and **49** (Scheme 15).

Glycosyl fluorides can also be prepared from glycosyl chlorides in two steps. Treat

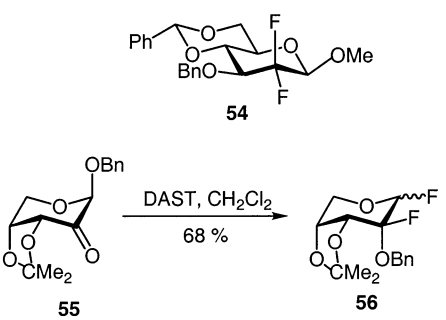


Scheme 15.

ment of the chloride **50** with AgF gave the fluoride **51** in a low yield (40%), whereas treatment of the chloride **50** first with AgOTf in CH_3CN then with DAST in CH_2Cl_2 (at -78 °C) gave the fluoride **51** in 98% overall yield [29] (Scheme 16).



Scheme 17.



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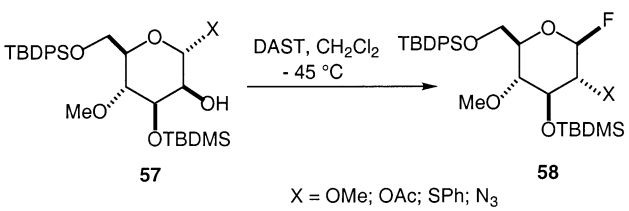
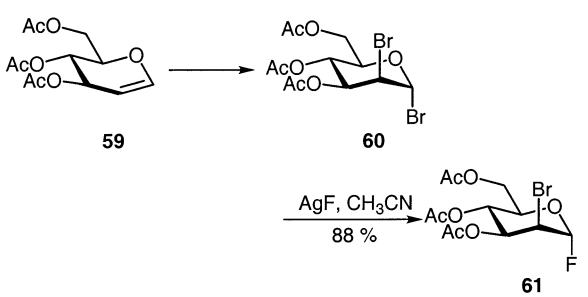


Scheme 19.



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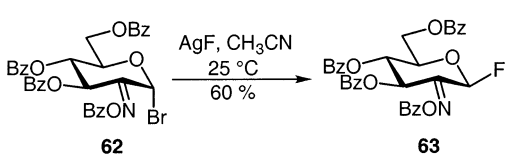


Scheme 21.

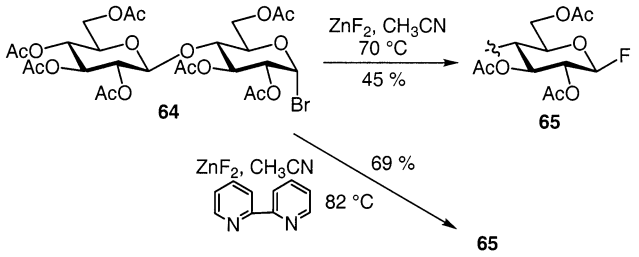
Not only monofluorinated compounds but also *gem*-difluorinated compounds have received wide attention in the carbohydrate field. Generally, *gem*-difluorinated compounds can be obtained from uloses with DAST, but treatment of 2-uloses with DAST often gave 1-fluorides, as exemplified by the reaction of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-2-ulose (**52**) giving **53** through methoxy group migration [30] (Scheme 17). When the β anomer of **52** was used, the methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2,2-difluoro derivative **54** was obtained. The 1,2-migration took place only when the anomeric group had axial orientation. Likewise, *O*-benzyl derivative **55** was converted to the *vic*-difluoro compound **56** in 68% yield [31] (Scheme 18).

Nicolaou and co-workers have discovered a new synthetic technology for the stereocontrolled synthesis of 2-deoxy α- and β-glycosides using DAST [32]. That is: (1) introduction of fluorine at C-1; (2) introduction of *O*-, *S*- and *N*-containing substituents at C-2; (3) inversion of configuration at C-2; (4) deoxygenation at C-2; and (5) stereocontrolled synthesis of α- and β-glycosides. Compound **57** was allowed to react with excess DAST in CH_2Cl_2 at -45 °C to afford the glycosyl fluoride **58** in high yields (Scheme 19).

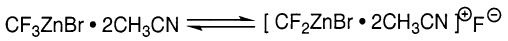
2.3 Metal fluorides (MF_n).

Metal fluorides have been employed to transform glycosyl bromides and chlorides into glycosyl fluorides through nucleophilic halide exchange. Silver fluoride is the most commonly used reagent for this purpose. 3,4,6-Tri-*O*-acetyl-2-bromo-2-deoxy-α-D-mannopyranosyl bromide (**60**), prepared in situ from the glycal **59**, was allowed to react with AgF in CH_3CN to give the corresponding mannopyranosyl fluoride **61** in 88% yield [33] (Scheme 20). 2-Benzoyloxyiminoglycosyl bromide (**62**) also gave the β-fluoride **63** in 60% yield, while the benzoyloxyimino group remained intact [34] (Scheme 21).

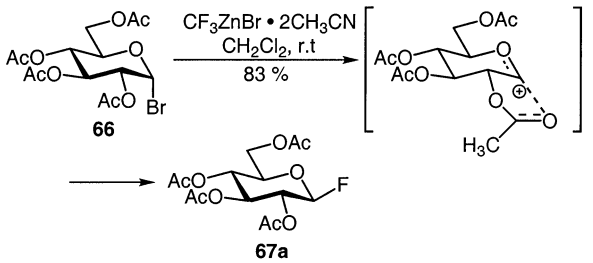
Treatment of acetyl-protected α-D-glucosyl bromides with zinc fluoride in MeCN gave the



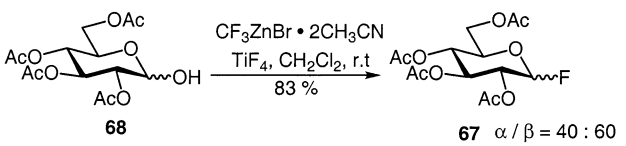
Scheme 22.



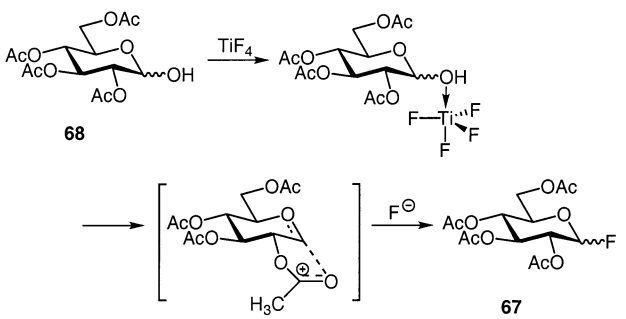
Scheme 23.



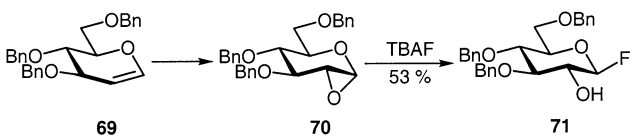
Scheme 24.



Scheme 25.



Scheme 26.



Scheme 27.

β-1-fluorides. Crystalline zinc fluoride is soluble in refluxing acetonitrile. Treatment of hepta-*O*-acetyl-α-D-cellobiosyl bromide (**64**) with ZnF_2 at high temperature [35] in the presence or absence of 2,2′-bipyridine gave a yield for **65** of 69 or 45%, respectively (Scheme 22). The precipitation of a 2,2′-bipyridine–$ZnBr_2$ complex from the reaction solution would reduce the concentration of bromide ions and would be followed by a shift of the equilibrium between bromides and fluorides.

Furthermore, trifluoromethylzinc bromide can be used as the fluorinating reagent of glycosyl bromides [36]. This reagent is assumed to exist in an equilibrium as shown in Scheme 23.

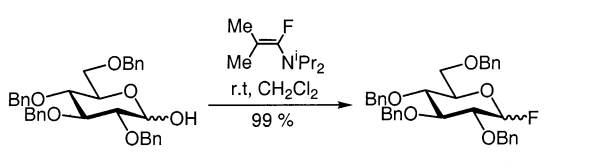
2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**66**) was allowed to react with this reagent to afford the corresponding fluoride **67a** in a β-selective manner (Scheme 24). This result can be explained by the presence of the oxonium ion intermediate with the anchimeric assistance of the acetyl group at C-2.

In addition, the replacement of a glycosidic OH group by fluorine was investigated by using this reagent. Under the same conditions as described for glycosyl bromide **66**, the reactions resulted in poor conversions. However, 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**68**), when treated with $CF_3ZnBr{\cdot}2CH_3CN$ and TiF_4 in dichloromethane, gave a mixture of the anomeric fluorides **67** in good yield (Scheme 25).

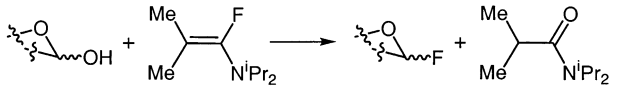
In this process, TiF_4 catalyzed the formation of the oxocarbenium ion intermediate as shown in Scheme 26.

2.4 Others.

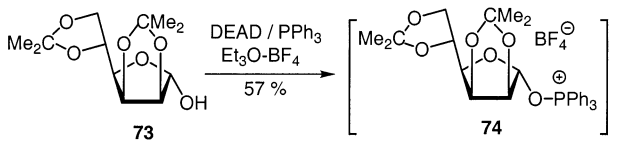
Tetrabutylammonium fluoride (TBAF) is utilized for the preparation of glycosyl fluorides from 1,2-anhydro-α-D-hexopyranose derivatives [37]. The perbenzylated 1,2-anhydro-α-D-hexopyranose **70**, prepared by epoxidation of the corresponding glycal **69**, was allowed to react with TBAF to afford the β-glycosyl fluoride **71** in 53% yield via an S_N2 pathway (Scheme 27).



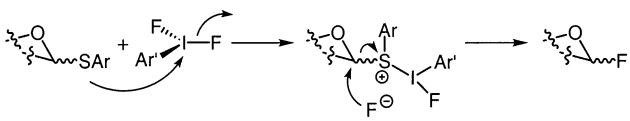
Scheme 28.



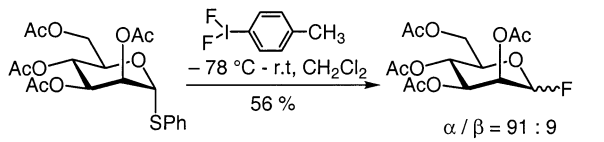
Scheme 29.



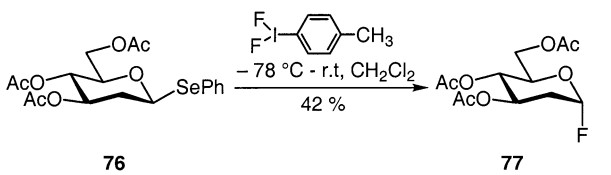
Scheme 30.



Scheme 31.



Scheme 32.



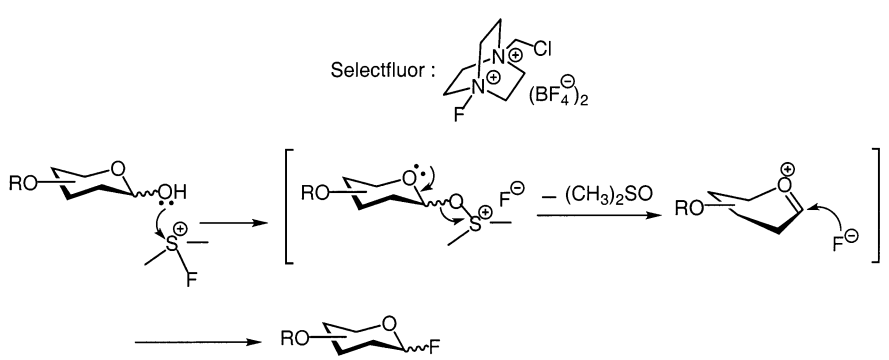
Scheme 33.

N,*N*-Diisopropyl(1-fluoro-2-methyl-1-propenyl)amine was found to be an effective reagent for the conversion of various furanose and pyranose hemiacetals into the corresponding glycosyl fluorides [38]. This reagent did no damage to several types of hydroxy-protecting groups such as benzyl, benzoyl, acetyl, acetonide, or silyl functionalities owing to the fluorination under neutral conditions. By the use of this reagent, 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl fluoride (**2**) was obtained from the corresponding hemiacetal **72** with the ratio of $\alpha/\beta = 7{:}18$ (Scheme 28). The reaction takes place in the manner as indicated in Scheme 29, on account of the presence of the only byproduct, *N*,*N*-diisopropylisobutyramide.

Modification of the Mitsunobu reaction allows one to also generate a glycosyl fluoride [39] (Scheme 30). By exposure to triphenyl phosphine, diethyl azodicarboxylate (DEAD) and triethyloxonium tetrafluoroborate ($Et_3O^+ BF_4^-$), 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**73**) was converted into the fluoride **75**. This reaction proceeds via the unstable oxyphosphonium salt **74**, which decomposes via the stabilized carbonium ion forming the fluoride **75**.

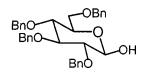
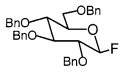
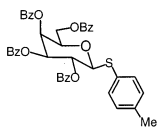
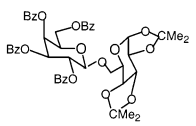
Furthermore, hypervalent iodoarenes like 4-methyl-(difluoroiodo)benzene may be used for the preparation of glycosyl fluorides from thioglycosides or selenoglycosides via the pathway shown in Scheme 31 [40].

When an axially arranged acetate exists in the 2-position, an intermediate oxocarbenium ion is stabilized by anchimeric assistance, and the attack of fluoride occurs from the axial side (Scheme 32). However, when an α-phenylthio derivative of tetra-*O*-benzyl-D-glucose was allowed to react with the reagent, it underwent S_N2 displacement to give the corresponding β-glycosyl fluoride. The reaction



Scheme 34.

Table 2
Synthesis of glycosyl fluorides using Selectfluor [a]

Entry	Sustrates	Conditions	Products	Yields (%)	α / β ratio
1		A		70	1 : 1
2		B		82	1 : 0
3		C		95	0 : 1

[a] A: Selectfluor (3 equiv), SMe_2/DMF (1:1), rt. B: Selectfluor (3 equiv), 4 Å MS, CH_3CN, 0 °C. C: Selectfluor (1.5 equiv), $BF_3{\cdot}Et_2O$ (1.5 equiv), donor (1.5 equiv), 4 Å MS, CH_3CN, 0 °C.

with the 2-deoxy-phenylselenoglycoside **76** was also examined [41]. Using the same reagent glycosyl fluoride **77** was formed via S_N2 inversion (Scheme 33).

Recently, Wong and co-workers have reported fruitful application of an electrophilic N–F fluorinating reagent, Selectfluor [(1-chloromethyl - 4 - fluoro - 1,4 - diazoniabicyclo-[2.2.2]-octane bis(tetrafluoroborate)] in carbohydrate chemistry [42]. The reagent is relatively inexpensive, safe and easy to handle.

The transformation of 1-hydroxy sugars to glycosyl fluorides was performed with a mixture of Selectfluor and methyl sulfide, presumably via a process as shown in Scheme 34. Moreover, Selectfluor can be used for the conversion of thioglycosides to glycosyl fluorides (Table 2). A plausible mechanism for thioglycoside activation and glycosylation is shown in Scheme 35.

3. Typical procedures

3.1 Fluorination with pyridinium poly(hydrogen fluoride) [12].

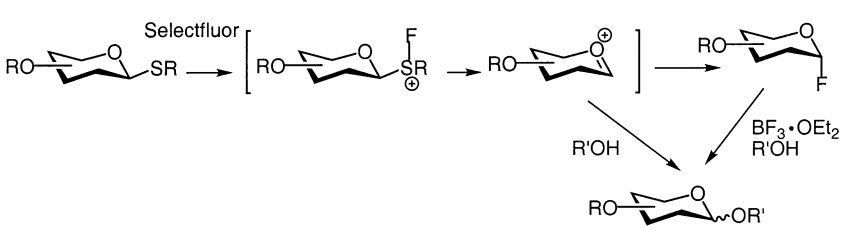
Pyridinium poly(hydrogen fluoride) [10] (4 mL) was added dropwise to an ice-cooled solution of 1,2-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-D-glucofuranoside (1.142 g, 2.5 mmol) in dry toluene (5 mL). The mixture was left to stand at 0 °C for 5 h. Ether (10 mL) and satd KI solution (30 mL) were added to the reaction mixture, which was then extracted with a 3:1 mixture of ether and hexane (3 × 30 mL). The combined extracts were then washed with satd KI solution (30 mL), satd Na_2CO_3 solution (30 mL), and brine (30 mL), dried (Na_2SO_4), filtered and evaporated under diminished pressure to give a white solid. Recrystallization from ethanol gave 2-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-β-D-glucofuranosyl fluoride (0.26 g, 30%).

3.2 Fluorination with DAST: general procedure [23].

To the alcohol (4.52 mmol) in a stirred solution of THF (12 mL) at −30 °C under argon gas was added 1.2 equiv of DAST. After removal of the cooling bath, stirring at room temperature for 20 min completed the reaction. The reaction mixture was cooled to −30 °C and methanol (0.3 mL) was added. The solution was neutralized with aq $NaHCO_3$ and extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated to yield a crude mixture of fluorides that was separated by column chromatography (1:1 hexanes–EtOAc).

3.3 Fluorination with trifluoromethylzinc bromide: general procedures [36].

Glycosyl bromide (3.4 mmol), trifluoromethylzinc bromide [43] (1.15 g, 5.4 mmol),



Scheme 35.

molecular sieves (3 Å) (0.4 g) and anhyd CH_2Cl_2 (40 mL) were placed in a polyethylene flask. After stirring for 12 h at rt, the mixture was agitated with satd aq $NaHCO_3$ solution (20 mL) and filtered. Subsequently, the organic phase was separated, washed with H_2O (2×10 mL) and dried (Na_2SO_4), and the solvent was evaporated under diminished pressure. The residue was purified by column chromatography.

*3.4 Fluorination with selectfluor; 2,3,4,6-tetra-*O*-benzyl-*D*-gluco-pyranosyl fluoride [42].*

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose (37 mg, 0.07 mmol) was dissolved in anhyd 1:1 DMF–SMe_2 (3 mL), and to this solution was added Selectfluor (78 mg, 0.21 mmol). After 5 min, the solution was diluted with 50 mL EtOAc, washed with water and brine, and dried over $MgSO_4$. Silica gel chromatography yielded the product (26 mg, 70%).

*3.5 5-*O*-Benzyl-2,3-*O*-isopropylidene-*D*-ribo-furanosyl fluoride [44].*

5-*O*-Benzyl-2,3-*O*-isopropylidene-D-ribofuranose (0.210 g, 1.0 mmol) was dissolved in anhyd 1:1 DMF–SMe_2 (10 mL), and to this solution was added Selectfluor (1.063 g, 3.0 mmol). After 5 min, the solution was treated in the same way as mentioned above to yield the corresponding α- and β-fluorides in 28 and 42% yields, respectively.

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