CLEAVAGE OF THE EPIMINES OF 1,6-ANHYDROHEXOSES WITH FLUORIDE ANION

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Aziridine ring cleavage reactions of five *N*-nosylepimines (**2**–**6**) having D-*talo*, D-*galacto*, D-*manno*, and D-*allo* configurations with potassium hydrogendifluoride under various reaction conditions have been performed. The cleavage regioselectively afforded diaxial isomers of vicinal amino-fluoro derivatives of 1,6-anhydro-β-D-gluco- and mannopyranose **7**–**11** in 51–94% yields. Removal of 2-nitrobenzenesulfonyl protecting group with benzenethiol has been attempted in the case of compound **10**.

Keywords: Cleavage reactions; Fluorine; NMR spectroscopy; Aziridines; Aminosugars; Anhydrosugars; Fluorosugars; Carbohydrates.

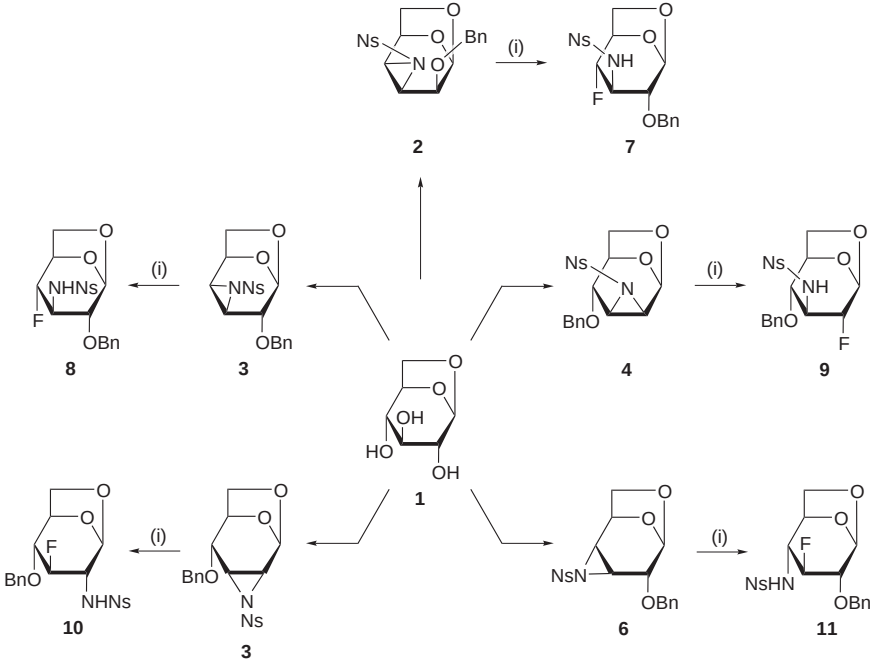
Carbohydrates substituted with fluorine represent[1,2] an important family of synthetic modifications of natural bioactive compounds in which fluorine atom modifies their biochemical[3–5] and pharmacological[6] properties or is used for radiolabelling[7] of natural compounds via carbohydrate substitution with ^{18}F (e.g. 2-deoxy-2-fluoro-D-glucose[8]). The introduction of fluorine into carbohydrate molecule can be accomplished by various methods, the nucleophilic displacement[9,10] and the cleavage of an oxirane[11–13] or aziridine[14–16] ring are the most common. We have recently[17,18] found out that *N*-tosylepimines of 1,6-anhydro-β-D-hexopyranoses react with halides by *trans*-diaxial cleavage and elaborated experimental conditions for aziridine ring cleavage with chloride, bromide and iodide anions resulting in regioselective formation of a single isomer of the corresponding sulfonamide.

However, attempts to cleave *N*-tosylepimines also with fluoride led only to the recovery of insufficiently reactive starting tosylepimines[19]. Therefore, we switched to 2-nitrobenzenesulfonyl activating group exploiting its higher reactivity[20] and smooth deprotection[21,22], since *N*-tosyl group is also known as difficult to cleave[23] (especially in the presence of a halogen atom in the molecule[24,25]). In this paper we present the aziridine ring cleavage

of *N*-2-nitrobenzenesulfonylated epimino derivatives (nosylepimines) of 1,6-anhydro-β-D-hexopyranoses with fluoride anion and subsequent *N*-deprotection of one of prepared sulfonamide (compound **10**) with benzenethiol.

RESULTS AND DISCUSSION

Starting nosylepimines **2**–**6** were prepared (Scheme 1) from 1,6-anhydro-β-D-glucopyranose (levoglucosan **1**, obtained by vacuum pyrolysis of starch according to a published procedure[26]) via a synthetic sequence[20,27] employing preparation of vicinal azidotosylates by azidolysis of 1,6:2,3- and 1,6:3,4-dianhydro-β-D-hexopyranoses and $NaBH_4$ reduction as the key steps for building of aziridine ring onto the sugar skeleton. Activating/protecting nosyl group was introduced by sulfonylation using 2-nitrobenzenesulfonyl chloride in a triethylamine–tetrahydrofurane mixture at –30 to –40 °C. Yields of the target nosylepimines were in the range 58–84%.



Bn = benzyl
Ns = 2-nitrobenzenesulfonyl

(i) KHF_2, $Bu_4N[Ph_3SnF_2]$, *N*-methylpyridinium tosylate

SCHEME 1

Cleavage of aziridine ring was attempted by various forms of fluoride anion. Utilization of neat tetrabutylammonium hydrogendifluoride[28] at 100 °C (as described in ref.[20] with 59% yield of **9**) was found to depend on reaction scale. We reached the reported yield on 0.1 mmol scale, but on 1 mmol scale the yield dropped to 7.5% due to the massive decomposition of the starting material. No way to improve it. Similar or worse yields were obtained for the rest of nosylepimines studied. Other reagents tried led to recovery of the starting material ((diethylamino)sulfur trifluoride, pyridinium polyhydrogenfluoride), to the complete decomposition of the reaction mixture (anhydrous TBAF, Bu_4NF, in acetonitrile) or yielded only small amounts of fluoro derivatives (33–38% in the reaction of **4** with melted KHF_2 at 240 °C, ref.[20]) thus demonstrating the very low reactivity of fluoride as a nucleophile.

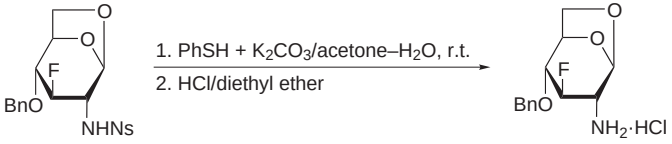
A difluorostannate complex $Bu_4N[Ph_3SnF_2]$ reported[29,30] as a successful replacement of KF and TBAF in nucleophilic substitution with fluoride was also tried with no detectable formation of fluoro derivatives at 150 °C. We therefore decided to use KHF_2 as the main nucleophile (due to available proton in the molecule necessary to complete the ring cleavage) and $Bu_4N[Ph_3SnF_2]$ as co-nucleophile (its role is transporting in the process of phase-transfer catalysis, cf. refs[29,31]) in an ionic-liquid solvent, *N*-methylpyridinium tosylate. The ionic-liquid solvent enables manipulation of all reagents and nosylepimines in solution in a wide range of temperatures. Optimal temperature for particular nosylepimine was estimated according its thermal instability and detectable (TLC) progress of the ring cleavage. Cleavage reactions without addition of *N*-methylpyridinium tosylate or in conventional dipolar aprotic solvent such as DMF or DMSO yielded only small amounts (up to 10%) of fluoro derivatives.

Under the optimal cleavage conditions, nosylepimines **2**–**6** afforded the corresponding fluoro derivatives **7**–**11** in the yields:75, 72, 94, 51, and 68%, respectively.

In all cases, the cleavage of the aziridine ring proceeded stereochemically in accordance with the Fürst–Plattner rule[32] prediction (*trans*-diaxial aziridine-ring opening). No diequatorial isomers were detected in the reaction mixtures.

Obtained sulfonamides can be easily deprotected by the treatment with benzenethiol and potassium carbonate in an acetone–water mixture as described earlier for the derivative **9** and some other halonosyl derivatives[20]. In contrary to the other halogens, the fluorine atom is stable in all positions of the 6,8-dioxabicyclo[3.2.1]octane skeleton showing no tendency to back-cyclize aziridine ring under slightly alkaline conditions of nosyl-group

deprotection (cf. ref.[20]). The stability was demonstrated on the fluoro derivative **10**, only compound **12** but no epimine was formed (Scheme 2).



10 **12**

SCHEME 2

The structure of fluoro derivatives **7**–**12** was determined by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy (for NMR data, see Tables I–III). Structure assignment was achieved using correlated homonuclear 2D-COSY and heteronuclear ^{1}H, ^{13}C-2D-HMQC spectra. The presence of fluorine was detected in ^{19}F NMR spectra (chemical shift in the range –179 to –183 ppm) and from ^{1}H NMR spectra due to typical H,F couplings: geminal 44–45 Hz, vicinal 8–14 Hz and long-range 1.1–5.5 Hz. Similarly C,F coupling constants could be estimated from ^{13}C NMR spectra: geminal 182–189 Hz, vicinal 20–32 Hz and long-range 5–8 Hz. The D-*gluco* configuration for **8**–**11** was assigned on the basis of typical values[13,33] for coupling constants: vicinal $J(2,3)$, $J(3,4)$, $J(4,5) \approx$ 1.1–1.9 Hz and long-range $J(1,3)$, $J(2,4)$, $J(3,5) \approx$ 0.5–1.8 Hz. The D-*manno* configuration of **7** manifested itself mainly by large coupling $J(2,3)$ = 6.4 Hz. Fluoro derivative **12** adopts the boat $B_{O,3}$ conformation as is indicated by higher values of couplings constants $J(2,3)$ = 5.2 Hz and $J(3,4)$ = 5.9 Hz (cf. ref.[20]).

CONCLUSION

A successful procedure for the aziridine ring-cleavage in epimino derivatives of 1,6-anhydrohexoses with fluoride is reported. The procedure utilizes hydrogendifluoride anion together with $Bu_4N[Ph_3SnF_2]$ as co-nucleophile in ionic-liquid environment and enables the preparation of sugar amino fluorides via aziridine-ring cleavage on preparative scale (hundreds of milligrams). Other conditions have been also tested, but without success (very low or zero yields of the cleavage products). The prepared nosylamides can be easily deprotected under the formation of stable hydrochlorides of fluoroamines.

TABLE I
^{1}H NMR (400 MHz) and ^{19}F NMR (376.3 MHz) chemical shifts (ppm) of compounds **7**, **8**, **10**, **11** ($CDCl_3$), and **12** (CD_3SOCD_3)

Comp.	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	OCH_2	NH	Arom. H	F
7	5.48	3.64	3.95	4.91	4.67	4.40	3.82	4.22 4.04	6.80	6.9–8.11	–182.3
8	5.43	3.15	3.82	4.53	4.72	4.10	3.76	4.44 4.21	5.86	7.25–7.89 8.17–8.22	–179.0
10	5.31	3.82	4.48	3.45	4.58	3.99	3.74	4.62 4.58	6.14	7.28–7.38 7.71–7.83 8.15–8.17	–180.9
11	5.41	3.40	4.46	3.89	4.45	4.09	3.74	4.57 4.48	6.40	7.24–7.37 7.71–7.82 8.15–8.17	–180.0
12	5.45	3.65	4.75	3.68	4.79	3.91	3.68	4.69	8.33 (NH_3^+)	7.42–7.31	–176.5

TABLE II

Coupling constants ($J_{H,H}$ and $J_{H,F}$ in Hz) of compounds **7**, **8**, **10**, **11**, and **12**

Comp.	*J*(1,2)	*J*(2,3)	*J*(3,4)	*J*(4,5)	*J*(5,6en)	*J*(5,6ex)	*J*(6en,6ex)	*J*(gem) (OBn)	*J*(N*H*,*x*) *x*=2,3,4	*J*(1,3)	*J*(2,4)	*J*(3,5)
7	<0.5	6.4	1.7	1.7	≈0	5.5	8.1	11.75	[a]	1.7	≈0	1.7
8	[a]	1.9	1.9	1.7	≈0	5.0	8.2	12.3	8.1	1.6	<0.5	1.6
10	2.4	1.8	1.8	1.1	1.1	5.65	7.8	12.2	10.4	1.8	1.5	1.8
11	1.8	1.8	1.8	[a]	1.1	5.6	7.8	12.2	10.0	1.8	1.8	1.8
12	<0.5	5.2	5.9	[a]	≈0	4.7	7.2	[a]	–	≈0	≈0	≈0

Comp.	*J*(1,F)	*J*(2,F)	*J*(3,F)	*J*(4,F)	*J*(5,F)	*J*(6ex,F)	*J*(6en,F)
7	≈0	≈0	8.7	44.0	8.7	5.5	<0.5
8	≈0	≈0	15.3	45.0	10.7	4.8	<0.5
10	≈0	13.1	44.4	13.1	<0.5	1.2	1.1
11	≈0	13.9	44.3	13.9	<0.5	1.2	1.1
12	≈0	14.3	34	27.5	≈0	≈0	≈0

[a] The value could not be determined.

TABLE III
^{13}C NMR data (100.8 MHz) of compounds **7**, **8**, **10**, **11** ($CDCl_3$), and **12** (CD_3SOCD_3)

Comp.	C-1	C-2	C-3	C-4	C-5	C-6	Other carbons
7	99.45	70.89	53.47 (32.4)	90.36 (182.3)	74.17 (19.5)	64.59 (7.6)	OBn: 71.71 (OCH_2), 130.57, 128.41 (2), 128.05, 127.32 (2) Ns: 147.50, 136.31, 133.47, 133.08, 132.63, 125.74
8	100.37	75.32	52.49 (29.8)	89.00 (189.0)	74.22 (21.70)	64.53 (8.4)	OBn: 71.71 (OCH_2), 131.15, 128.55 (2), 128.03 (2), 127.63 Ns: 148.50, 136.55, 134.02, 133.44, 131.60, 125.56
10	100.30	52.92 (25.5)	87.61 (186.6)	73.25 (26.3)	73.06	65.12 (4.6)	OBn: 71.60 (OCH_2), 130.17, 128.67 (2), 128.31, 127.95 (2) Ns: 147.60, 136.49, 134.86, 133.75, 133.15, 125.55
11	99.71	72.64 (23.2)	87.51 (186.9)	53.22 (28.3)	74.66	65.41 (5.3)	OBn: 72.42 (OCH_2), 129.99, 128.32, 127.96 (2), 128.63 (2) Ns: 147.61, 136.51, 135.09, 133.74, 133.11, 125.58
12	99.34	56.02	79.21	70.69	74.38	64.87	OBn: 73.14 (OCH_2), 137.66, 128.32 (2), 127.78 (2), 127.65

[a] $-J$(C,F) in Hz shown in parenthesis.

EXPERIMENTAL

Melting points were determined on a Boëtius melting-point microapparatus and are uncorrected. The optical rotations were measured on an Autopol III (Rudolph Research, Flanders (NJ), U.S.A.) polarimeter at 23 °C and are given in 10^{-1} deg cm^2 g^{-1}. The ^{1}H and ^{13}C NMR spectra were measured on a Varian INOVA-400 (^{1}H at 400 MHz and ^{13}C at 100 MHz) instrument in $CDCl_3$ (referenced to TMS for ^{1}H and the chloroform signal at δ 77.0 ppm for ^{13}C) at 25 °C. Correlated 2D techniques were used for the structural assignments. High-resolution mass spectra were recorded on a ZAB-EQ (VG Analytical, U.K.) instrument using the FAB method (Xe ionization). TLC was carried out on MERCK DC Alufolien with Kiesegel F_{254} with hexane–ethyl acetate (3:2) solvent systems. TLC plates were visualized by UV detection at 254 nm and with an anisaldehyde solution in sulfuric acid. Column chromatography was performed on silica gel 60 MERCK (70–230 mesh ASTM) with hexane–ethyl acetate gradient. The solvents were evaporated on a vacuum rotary evaporator at 40 °C (unless stated otherwise). Petroleum ether refers to the 40–60 °C distillation fraction. Reactions were carried out under argon atmosphere. Starting epimines **2**–**6** were prepared using the published procedures (2,3-epimines[20], 3,4-epimines[27]). $Bu_4N[Ph_3SnF_2]$ was prepared according to refs[29,30]. *N*-Methylpyridinium tosylate was prepared by mixing of commercially available methyl tosylate with an equivalent of dry pyridine at room temperature and drying of the resulting solid in a vacuum desiccator over P_2O_5. The ^{1}H and ^{19}F NMR spectral parameters are given in Tables I and II, and those of ^{13}C NMR spectra in Table III.

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-4-fluoro-3-(*N*-2-nitrobenzene-1-sulfonamido)-β-D-mannopyranose (**7**)

Epimine **2** (211 mg, 0.50 mmol), KHF_2 (40 mg, 0.51 mmol), $Bu_4N[Ph_3SnF_2]$ (352 mg, 0.55 mmol), and *N*-methylpyridinium tosylate (600 mg, 2.3 mmol) were mixed and placed in a silicon oil bath where the mixture melted and the temperature was maintained at 115 °C for 60 min. The brown mixture was cooled to room temperature and triturated with EtOAc (4 ml). The resulting suspension was partitioned between water (30 ml) and dichloromethane (60 ml). The extract was washed with 5% aqueous $NaHCO_3$, water and dried over anhydrous Na_2SO_4. After evaporation of dichloromethane, the residue was chromatographed on silica gel (25 g, hexane–EtOAc 3:2) to afford fluoro derivative **7**. Yield 167 mg (75%, EtOAc–Et_2O–petroleum ether); m.p. 157–159 °C; $[\alpha]_D$ –195 (*c* 0.28, $CHCl_3$). For $C_{19}H_{19}FN_2O_7S$ (438.4) calculated: 52.05% C, 4.37% H, 4.33% F, 6.39% N, 7.31% S; found: 52.12% C, 4.34% H, 3.96% F, 6.20% N, 7.43% S.

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-4-fluoro-3-(*N*-2-nitrobenzene-1-sulfonamido)-β-D-glucopyranose (**8**)

The same amounts of the epimine (**3**, 211 mg) and other reagents were worked up as is described for the preparation of compound **7**. The reaction proceeded at 100–110 °C for 4 h. Yield 160 mg of **8** (72%, EtOAc–Et_2O–petroleum ether); m.p. 59–60 °C; $[\alpha]_D$ –61 (*c* 0.17, $CHCl_3$). For $C_{19}H_{19}FN_2O_7S$ (438.4) calculated: 52.05% C, 4.37% H, 4.33% F, 6.39% N, 7.31% S; found: 52.02% C, 4.39% H, 4.01% F, 6.26% N, 7.45% S.

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-2-fluoro-3-(*N*-2-nitrobenzene-1-sulfonamido)-β-D-glucopyranose (**9**)

Epimine **4** (293 mg, 0.7 mmol), KHF_2 (40 mg, 0.7 mmol), $Bu_4N[Ph_3SnF_2]$ (485 mg, 0.77 mmol), and *N*-methylpyridinium tosylate (800 mg, 3 mmol) were mixed and placed in a silicone oil bath heated at 130 °C where the mixture melted. The temperature was lowered to 100 °C and maintained for 6 h. The brown mixture was further worked up as described for the derivative **7** to afford fluoroamine **9**. Yield 290 mg (94%, EtOAc–Et_2O–petroleum ether); m.p. 181–183 °C. The prepared compound was identical (^1H and ^{19}F NMR data) with a sample already reported in literature[20].

1,6-Anhydro-4-*O*-benzyl-3,4-dideoxy-3-fluoro-2-(*N*-2-nitrobenzene-1-sulfonamido)-β-D-glucopyranose (**10**)

Epimine **5** (293 mg, 0.7 mmol), KHF_2 (40 mg, 0.7 mmol), $Bu_4N[Ph_3SnF_2]$ (485 mg, 0.77 mmol), and *N*-methylpyridinium tosylate (800 mg, 3 mmol) were mixed and placed in a silicon oil bath warmed at 140 °C where the mixture melted. The temperature was maintained for 2 h. The brown mixture was further worked up as described for compound **7** to afford fluoroamine **10**. Yield 157 mg (51%, EtOAc–Et_2O–petroleum ether); m.p. 98–101 °C; $[\alpha]_D$ –19 (*c* 0.28, $CHCl_3$). For $C_{19}H_{19}FN_2O_7S$ (438.4) calculated: 52.05% C, 4.37% H, 4.33% F, 6.39% N, 7.31% S; found: 52.17% C, 4.36% H, 4.16% F, 6.14% N, 7.30% S.

1,6-Anhydro-2-*O*-benzyl-2,3-dideoxy-3-fluoro-4-(*N*-2-nitrobenzene-1-sulfonamido)-β-D-glucopyranose (**11**)

The same amounts of the epimine (**6**; 293 mg) and other reagents were worked up as is described for the preparation of compound **10**. The reaction proceeded 5 h. Yield 208 mg of **11** (68%, EtOAc–Et_2O–petroleum ether); m.p. 49–51 °C; $[\alpha]_D$ –24 (*c* 0.19, $CHCl_3$). For $C_{19}H_{19}FN_2O_7S$ (438.4) calculated: 52.05% C, 4.37% H, 4.33% F, 6.39% N, 7.315 S; found: 52.11% C, 4.39% H, 4.44% F, 6.29% N, 7.41% S.

Deprotection with Benzenethiol. Typical Procedure

A fluoro derivative (0.1-mmol scale), potassium carbonate (10 equiv.), acetone (3 ml), benzenethiol (3 equiv.) and water (0.3 ml) were mixed up and stirred at room temperature until the starting fluoro derivative disappeared (45 min, TLC monitoring in a methanol–ethyl acetate 1:2). The yellow suspension was filtered through a pad of celite, celite washed with ethanol (30 ml) and combined filtrates were concentrated to yellow oil. The oil was chromatographed on silica gel (15 g, EtOAc–EtOH gradient elution) to afford free amine. The amine was dissolved in ethanol (1 ml) and a 1.4 M HCl solution in diethyl ether (1 ml) was added to form the corresponding hydrochloride. Resulting mixture was evaporated under diminished pressure and solid (or oily) residue was dried in vacuum desiccator over P_2O_5.

2-Amino-1,6-anhydro-4-O-benzyl-2,3-dideoxy-3-fluoro-β-D-glucopyranose hydrochloride (**12**). Prepared from **10** (67 mg, 0.151 mmol), K_2CO_3 (210 mg, 1.51 mmol) and benzenethiol (46 μl, 0.45 mmol). Yield 42 mg (95%); $[\alpha]_D$ –18.5 (*c* 0.46, MeOH). HR MS (FAB): calculated for $C_{13}H_{17}FNO_3$ 254.1193, found: 254.1180 (M^+).

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