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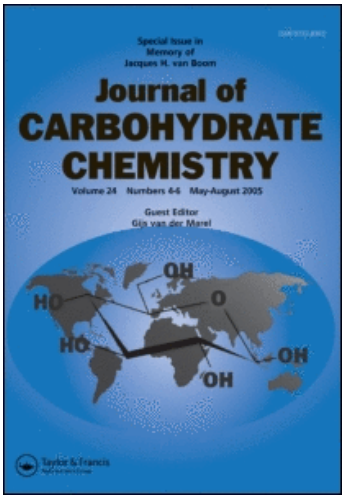

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J. CARBOHYDRATE CHEMISTRY, 6(2), 203-219 (1987)

REACTIONS OF PER-O-ACETYLATED CARBOHYDRATE TRIFLATES WITH HALIDE IONS[1]

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ABSTRACT

The reactions of bromide, chloride, and iodide ions with 1,3,4,6-tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-α-D-glucopyranose (2) and with 1,3,4,6-tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-β-D-mannopyranose (3) gave good to excellent yields of the corresponding deoxyhalogeno sugars. In contrast, when the gluco triflate 2 and tetrabutylammonium fluoride were heated under reflux in benzene, only 5-(acetoxymethyl)-2-formylfuran (13) was formed. Reaction of the manno triflate 3 under similar conditions produced 1,3,4,6-tetra-O-acetyl-2-deoxy-2-fluoro-β-D-glucopyranose (17), 1,3,4,6-tetra-O-acetyl-2-deoxy-β-D-erythro-hex-2-eno-pyranose (18), 4,6-di-O-acetyl-1,5-anhydro-2-deoxy-D-erythro-hex-1-enitol-3-ulose (19), and 1,2,3,4,6-penta-O-acetyl-β-D-glucopyranose (20). The mechanisms of the reactions of the triflates 2 and 3 with fluoride ion are discussed.

INTRODUCTION

Over the past several years we have been involved in a systematic study of the displacement reactions of the trifluoromethylsulfonyloxy (triflyloxy) group in carbohy-

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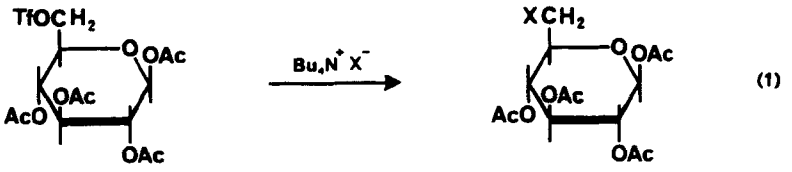
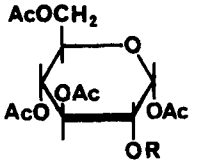
drate systems.[1-6] A recent paper on this topic described the reaction of 1,2,3,4-tetra-O-acetyl-6-O-(trifluoromethylsulfonyl)-β-D-glucopyranose (1) with halide ions (Equation 1).[3] The present study extends this investiga-



1 (1)

tion to include two per-O-acetylated triflates from which displacement should be considerably more difficult. The two compounds selected were 1,3,4,6-tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-α-D-glucopyranose (2) and 1,3,4,6-tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-β-D-mannopyranose (3). Compounds 2 and 3 were selected not



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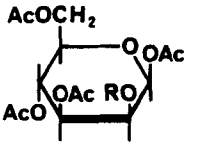
4 R=H



3 R=Tf
5 R=H

only to provide basic information about triflate reactivity but also as possible intermediates in the synthesis of unprotected 2-deoxy-2-halogeno sugars.

RESULTS AND DISCUSSION

The triflates 2 and 3 were prepared by treating the corresponding partially protected sugars (4 and 5, respec-

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tively) with triflic anhydride in dichloromethane at 0 °C. Displacement reactions involving compounds 2 and 3 were conducted by dissolving the triflate selected for study (2 or 3) in benzene, adding the appropriate tetrabutylammonium halide, and heating the reaction mixture under reflux for two hours. Product isolation was accomplished by chromatography on silica gel.

Reaction of 2 or 3 with tetrabutylammonium bromide or chloride (Equations 2 and 3) gave excellent yields of the corresponding substitution products (Table 1).

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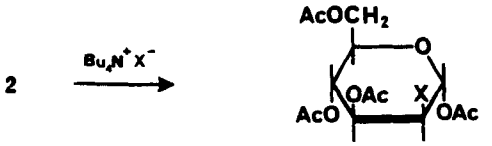
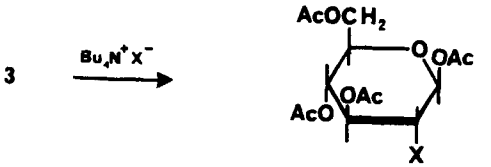


(2)

6 X = Br
7 X = Cl



(3)

8 X = Br
9 X = Cl
12 X = I

Surprisingly, however, treatment of compound 2 with tetrabutylammonium iodide gave a mixture of 1,3,4,6-tetra-O-acetyl-2-deoxy-2-iodo-α-D-mannopyranose (10) and 3,4,6-tri-O-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol

TABLE 1

Product Yields From Reactions of Triflates

2 and 3 with Tetrabutylammonium Halides

Triflate	Halide	Product	% Yield
2	Br	6	87
2	Cl	7	90
2	I	10[a]	51
2	F	13[b]	--
3	Br	8	89
3	Cl	9	86
3	I	12	92
3	F	17[c]	23

a. Compound 11 also was formed.

b. No deoxyfluoro sugar was produced. Only 5-(acetoxymethyl)-2-formylfuran (13) was formed.

c. Compounds 18-20 also were produced.

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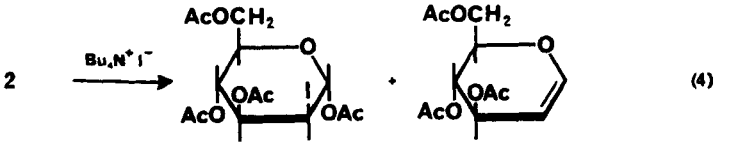
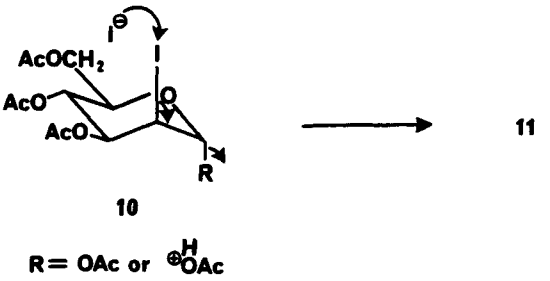
(11) (Equation 4). TLC analyses of the reaction mixture during reaction suggested that the iodide 10 was an intermediate in the formation of 11. This suggestion was supported by the observation that 11 continued to be formed



10 11



Scheme 1

slowly even after the triflate (2) had been consumed. Addition of a catalytic amount of acid to the reaction mixture after the triflate had reacted, caused an increase in the rate of formation of 11. These results suggest the reaction mechanism shown in Scheme 1 for the formation of 3,4,6-tri-O-acetyl-D-glucal (11). They further indicate that, as expected, protonation of the anomeric acetyl group (Scheme 1) facilitates reaction.

Treatment of the triflate 3 with tetrabutylammonium iodide gave only 1,3,4,6-tetra-O-acetyl-2-deoxy-2-iodo-β-D-glucopyranose (12) (Equation 3). The deoxyiodo sugar 12 would not be expected to undergo an elimination reaction similar to that observed for 10 since the trans periplaner arrangement of the departing groups found in compound 10 and required in an E2-like elimination reaction would be difficult for compound 12 to achieve (Scheme 2).

The use of triflate displacement reactions for the synthesis of deoxyfluoro sugars has received a great deal

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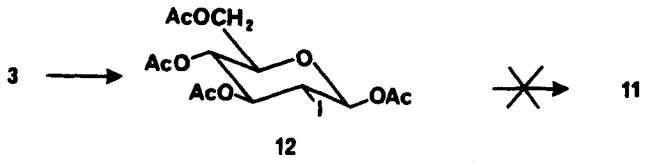

Scheme 2

of attention recently due to the biochemical and medicinal applications[7] possible for these compounds; thus, it was of particular interest to determine whether triflate displacement from compounds 2 and 3 could be used to prepare deoxyfluoro sugars.[8] Displacement reactions involving fluoride ion often occur with difficulty due to the reduced nucleophilicity of this heavily solvated ion.[9] Reactions in the presence of fluoride ion also are frequently accompanied by elimination processes due to the relatively high basicity of this ion.[10,11]

Treatment of the triflate 2 with tetrabutylammonium fluoride afforded no deoxyfluoro sugar; rather, only 5-(acetoxymethyl)-2-formylfuran (13) was formed. Although no mechanistic study was conducted on this reaction, a possible mechanism is shown in Scheme 3. Formation of 13 is thought to begin by attack of fluoride ion on the carbonyl carbon of the anomeric acetoxy group. This type of reaction may occur between fluoride ion and other carbonyl carbons in the molecule; however, for non-anomeric groups reaction is reversible and leads to no observable

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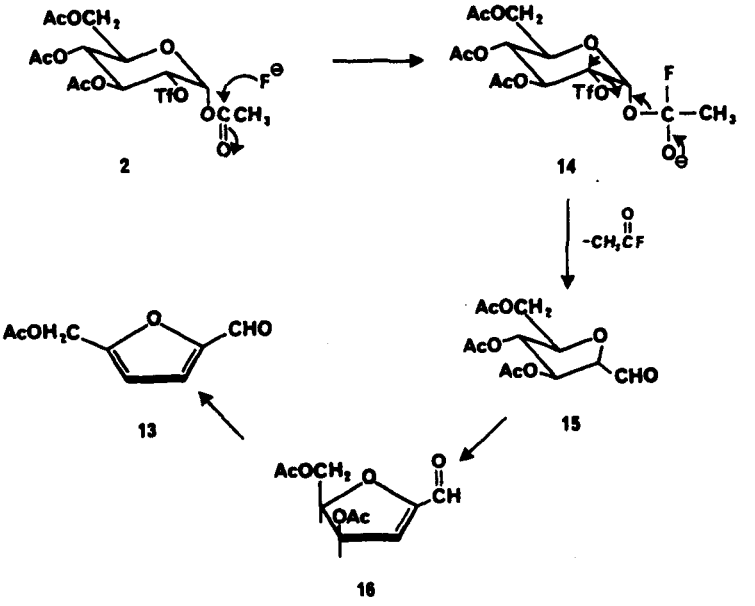

Scheme 3

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change. Only attack on the anomeric acetoxy group generates an intermediate (14) which has available a pathway other than simple fluoride ion expulsion; thus, 14 experiences an irreversible, ring contraction to give the aldehydo compound 15 (Scheme 3). In support of this proposed role for fluoride ion is the observation that no 5-(acetoxymethyl)-2-formylfuran (13) was formed when tetrabutylammonium fluoride was omitted from the reaction mixture.

Once compound 15 is formed, two successive eliminations of the elements of acetic acid generate the furan derivative 13. The driving force for the first elimination is thought to be the stability gained by formation of

the α,β-unsaturated aldehyde 16 while the second reaction, that is, conversion of 16 into the furan 13, produces an even more stable system due to formation of an aromatic compound (13).

Reaction of the manno triflate 3 with tetrabutylammonium fluoride gave the desired displacement product 1,3,4,6-tetra-O-acetyl-2-deoxy-2-fluoro-β-D-glucopyranose (17) in low yield (Table 1). Compound 17 was accompanied by 1,3,4,6-tetra-O-acetyl-2-deoxy-β-D-erythro-hex-2-enopyranose (18), 4,6-di-O-acetyl-1,5-anhydro-2-deoxy-D-erythro-hex-1-enitol-3-ulose (19), and 1,2,3,4,6-penta-O-acetyl-β-D-glucopyranose (20). A proposed mechanism for the formation of these compounds is shown in Scheme 4. The unsaturated compound 18 is the product of an E2 elimination from the triflate 3. Further reaction of 18 with fluoride ion results in a second elimination to give the α,β-unsaturated ketone 19. The proposal that 19 is produced from 18 is supported by the observation that 18 is converted into 19 under the reaction conditions. The pentaacetate 20 arises from reaction of the triflate 3 with acetate ion generated by the elimination reactions. In agreement with this proposal is the observation that 3 reacts with tetrabutylammonium acetate to give compound 20.

In conclusion, the results from reactions of the triflates 2 and 3 with tetrabutylammonium halides can be

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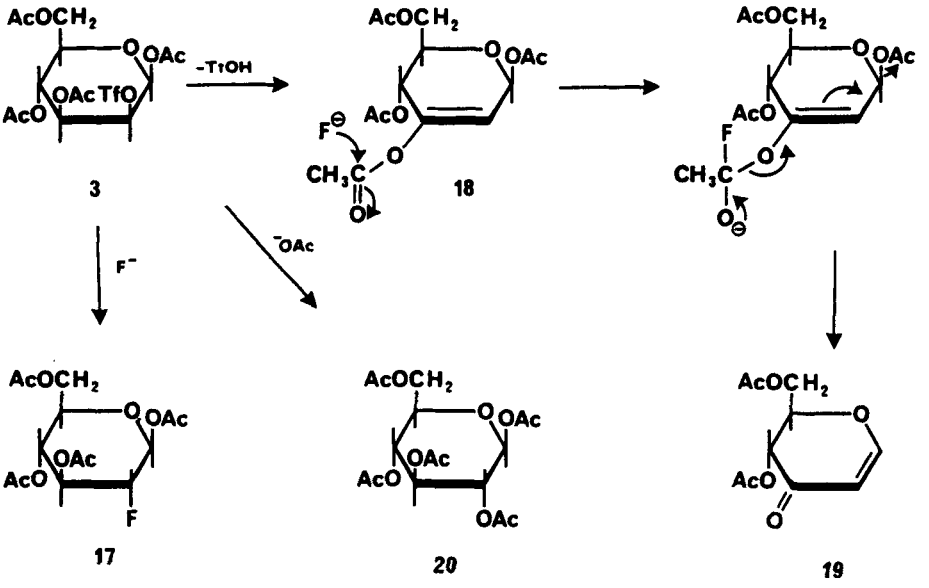

Scheme 4

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summarized in the following manner. The displacement of the triflyloxy group from the 2-position in these compounds (2 and 3) by halide ions occurs in good to excellent yields except when fluoride ion is used. The reduced nucleophilicity and increased basicity of this ion, when compared to other halides, causes competing elimination reactions to occur. Interestingly, no neighboring group participation was observed, even though this was a possible process, particularly for compound 3.

EXPERIMENTAL

General Procedures. ^{1}H NMR data (Table 2) were acquired using either a Varian T-60 or a Varian FT-80A spectrometer. ^{13}C NMR data (Table 3) were obtained from a

Table 2: ^{1}H-NMR Parameters

Cmpd.	H-1	H-2	H-3	H-4	H-5	H-6	H-6'	OC(O)CH_3
2	6.26 $J_{1,2}$=4	4.86 $J_{2,3}$=9	5.67----	5.06	4.43----------		3.80	1.98, 2.16 2.02 (6H)
3	5.92 $J_{1,2}$<1	5.33----------		5.07	4.27----------		3.63	2.02, 2.04 2.07, 2.12
6	6.26 $J_{1,2}$=2	4.40 $J_{2,3}$=4	5.14 $J_{3,4}$=$J_{4,5}$=10	5.45	5.45----------		3.77	2.03, 2.13 2.07 (6H)
7	6.13 $J_{1,2}$=2	4.31 $J_{2,3}$=3	5.63----	5.10	4.23----------		3.80	1.99, 2.10 2.03 (6H)
8	5.86 $J_{1,2}$=9	3.88 $J_{2,3}$=$J_{4,5}$=9.5	5.00	5.40 $J_{5,6}$=4	3.95 $J_{5,6'}$=2	4.33 $J_{6,6'}$=12.5	4.03	1.98, 2.02 2.05, 2.13
9	5.79 $J_{1,2}$=0	3.90 $J_{2,3}$=$J_{4,5}$=9	5.03 $J_{5,6}$=4.5	5.36	3.95 $J_{5,6'}$=2	4.38 $J_{6,6'}$=12.5	4.08	2.07, 2.10 2.13, 2.22
10	6.33 $J_{1,2}$=1	4.70-----4.40		5.48	4.27----------		3.67	2.03, 2.13 2.07 (6H)
12	5.47 $J_{1,2}$=8.5	3.74 $J_{2,3}$=$J_{4,5}$=9.5	4.91	5.30 $J_{5,6}$=4	3.82 $J_{5,6'}$=2	4.28 $J_{6,6'}$=12	3.98	1.95, 2.00 2.13, 2.22
13			7.20 $J_{3,4}$=3.5	6.59		5.17		2.18
17	5.72 $J_{1,2}$=8.2 $J_{5,6'}$=2.5	4.97 $J_{2,3}$=9.0	5.00 $J_{3,4}$=$J_{4,5}$=9.5 $J_{6,6'}$=12.5	5.41 $J_{5,6}$=4.5 $^1J_{HF}$=3.2	3.82 $^2J_{HF}$=43	4.25	4.05 $^3J_{HF}$=3	1.97, 2.01 2.13, 2.22
18	6.40 $J_{1,2}$=3	5.64 $J_{1,4}$=0.6	$J_{2,4}$=0.5	5.23 $J_{4,5}$=1.4	4.18	4.18	4.18	1.95, 1.98 (6H) 2.03
19	7.35 $J_{1,2}$=6	5.47		5.53 $J_{4,5}$=13	4.56 $J_{5,6}$=$J_{5,6'}$=3	4.40	4.32 $J_{6,6'}$=17	2.11, 2.18

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Table 3: ^{13}C-NMR Parameters

	2	3	6	7	8	9	10	12	13	17	18	19
C-1	88.14	88.83	93.21	92.94	92.69	92.89	94.76	93.95		91.02	88.14	162.43
C-2	79.59	81.35	47.94	56.44	47.36	56.94	27.20	25.80	152.73	88.02	115.25	105.40
C-3,C-4	69.75	73.12	71.35	71.23	73.94	74.01	71.49	75.23	121.41	72.49	145.71	187.44
	69.15	69.41	68.86	69.27	72.38	72.48	68.69	72.99	112.37	67.42	74.56	78.31
C-5	67.72	64.53	65.70	64.97	68.25	68.09	67.11	68.56	155.30	72.51	63.94	68.10
C-6	61.05	61.53	61.92	61.92	61.06	61.11	61.89	61.50	57.64	61.15	62.86	61.47
$-\underset{\underset{O}{\|\|}}{C}-CH_3$	170.46	170.29	170.60	170.62	169.98	170.10	170.66	170.44	170.11	170.32	170.40	169.17
	169.71	169.66	169.99	170.06	169.06	169.29	169.89	169.40		169.64	170.26	170.31
	169.29	168.94	169.26	169.26	169.00	169.11	169.29	168.44		169.31	169.49	
	168.04	167.73	168.08	168.07	168.07	168.26	168.14			168.60	168.59	
$-C\underset{\underset{O}{\|\|}}{C}H_3$	20.61	20.28	20.68	20.84	20.22	20.30	20.83	20.65	20.48	20.67	21.13	20.60
	20.46	20.18		20.67	20.09	20.15	20.70	20.52		20.42	20.82	20.44
	20.37	20.06					20.61				20.70	
CF_3	118.38	118.25										
	$^1J_{CF}$=319.6											
CHO									177.62			

Varian FT-80A spectrometer. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Chromatography was done on a 2.5 x 10 cm column of 230-400 mesh silica gel with a 3:2 ratio of ethyl ether-hexane. The column effluent was monitored by an ISCO UA-2 UV analyzer. Tetrabutylammonium halides remained on the column. Dichloromethane was distilled from phosphorus pentoxide and stored over 4A molecular sieve. Pyridine was distilled from barium oxide and stored over potassium hydroxide. Tetrabutylammonium salts were purchased from the Aldrich Chemical Company.

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Syntheses of 1,3,4,6-Tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-α-D-glucopyranose (2) and 1,3,4,6-Tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-β-D-mannopyranose (3). The appropriate tetraacetate [1,3,4,6-tetra-O-acetyl-α-D-glucopyranose[12] (4) or 1,3,4,6-tetra-O-acetyl-β-D-mannopyranose[13] (5)] (0.96 g, 2.75 mmol) and pyridine (0.58 mL, 7.17 mmol) were dissolved in 20 mL of dichloromethane. Triflic anhydride (0.85g, 3.0 mmol) was added to the reaction mixture which had been cooled to 0 °C. This mixture was stirred and allowed to warm to room temperature over a period of two h. The reaction mixture was then poured into 150 mL of cold saturated $NaHCO_3$ in a separatory funnel and shaken. The aqueous portion was extracted with three 25 mL portions of dichloromethane. The combined organic solutions were washed with 40 mL of

1% HCl and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give 1,3,4,6-tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-α-D-glucopyranose (2), mp 85.5-86.5 °C (hexane), or 1,3,4,6-tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-β-D-mannopyranose (3), mp 118-119 °C (hexane). NMR spectral data for compounds 2 and 3 are found in Tables 2 and 3. These triflates usually were reacted immediately since they decomposed slowly at room temperature. They are stable for months at -20 °C.

Syntheses of 1,3,4,6-Tetra-O-acetyl-2-deoxy-2-halogeno-β-D-glucopyranoses 8, 9, and 12. The triflate 3 (0.593 g, 1.70 mmol) was combined with the appropriate tetrabutylammonium halide (3.34 mmol) in 30 mL of anhydrous benzene and heated at reflux for two h. After cooling to room temperature, the benzene was removed under reduced pressure. The residue was dissolved in the minimum amount of dichloromethane, chromatographed as described in the general procedures, and recrystallized from ethanol. The reaction products (8, 9, and 12) were identified by analysis of their NMR spectra (Tables 2 and 3) and mp comparison with values reported in the literature: compound 8, mp 95-96 °C (lit.[14] mp 95-96 °C); compound 9, mp 110-111 °C (lit.[15] mp 108-110 °C); compound 12, mp 113.5-114.5 °C. Since compound 12 was previously unreported, its elemental analysis was determined. Anal. Calcd For $C_{14}H_{19}IO_9$: C, 36.70; H, 4.18. Found: C, 36.64: H, 4.31.

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Syntheses of 1,3,4,6-Tetra-O-acetyl-2-deoxy-2-halogeno-α-D-mannopyranoses 6, 7, and 10; 3,4,6-tri-O-acetyl-1,6-anhydro-2-deoxy-D-arabino-hex-1-enitol (11); and 5-(acetoxymethyl)-2-formylfuran (13). Syntheses of 6, 7, and 10 were conducted in a manner identical to the preparation of 1,3,4,6-tetra-O-acetyl-2-deoxy-2-halogeno-β-D-glucopyranoses 8, 9, and 12 except that the triflate 2 was the starting material. Yields for these products (6, 7, and 10), none of which crystallized, are given in Table 1. Compounds 6 and 7 were identified by analysis of their NMR spectra (Tables 2 and 3) and by comparison of these spectral data with those reported in the literature.[16,17] Compound 10 was identified by analysis of its NMR spectra and its elemental analysis. Anal. Calcd For $C_{14}H_{19}IO_9$: C, 36.70; H, 4.18. Found: C, 36.98; H, 4.01.

Reaction of 2 with tetrabutylammonium iodide yielded, in addition to the deoxyiodo sugar 10, 3,4,6-tri-O-acetyl-1,5-anhydro-2-deoxy-D-arabino-hex-1-enitol (11). Reaction of 2 with tetrabutylammonium fluoride resulted only in formation of 5-(acetoxymethyl)-2-formylfuran (13). Both compounds 10 and 13 were identified by comparison of their ^1H NMR spectra with authentic samples.[18]

Reaction of 1,3,4,6-Tetra-O-acetyl-2-O-(trifluoromethylsulfonyl)-β-D-mannopyranose (3) with Tetrabutylammonium Fluoride. Reaction of the triflate 3 with tetrabutylammonium fluoride was conducted in the manner de-

scribed for reaction of 3 with other halide ions. Chromatography described in the general procedures produced 1,3,4,6-tetra-O-acetyl-2-deoxy-2-fluoro-β-D-glucopyranose (17, 23% yield), identified by analysis of its NMR spectra (Tables 2 and 3) and comparison of the ^{1}H NMR spectral data with those reported in the literature.[11] In addition, 1,3,4,6-tetra-O-acetyl-2-deoxy-β-D-erythro-hex-2-enopyranose (18), 4,6-di-O-acetyl-1,5-anhydro-2-deoxy-D-erythro-hex-1-enitol-3-ulose (19, 23%), and 1,2,3,4,6-penta-O-acetyl-β-D-glucopyranose (20, 11%) were formed. Compound 20 was identified by ^{1}H NMR spectral comparison with an authentic sample.[18] The identification of compounds 18 and 19 was accomplished by analysis of their NMR spectra (Tables 2 and 3). The yield of 18 varied considerably from one experiment to the next because it hydrolyzed readily into 19; in fact, 18 was never isolated completely free of contamination by 19. Compound 19 was isolated in a pure state and subjected to elemental analysis. Anal. Calcd. for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30. Found: C, 52.39, H, 5.51.

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