# Intramolecular Reactions of Carbohydrate Triflates

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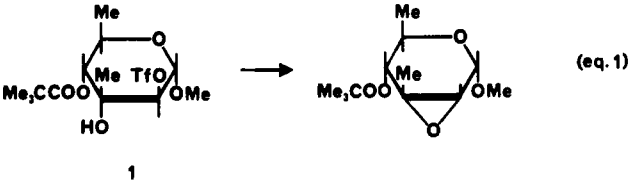
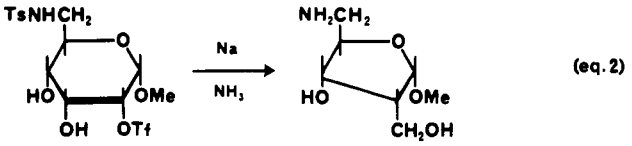
Each of the four possible methyl 2,6-dideoxy-β-D-hexopyranosides (**3–6**) was treated with an equivalent amount of triflic anhydride in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (**7**). The *ribo* isomer **3** produced both the 3-*O*-triflyl (**8**, 15%) and the 4-*O*-triflyl (**9**, 73%) derivatives while the *lyxo* isomer **4** gave only the 3-*O*-triflyl compound (**11**, 84%). Upon heating, the triflate **8** lost the elements of triflic acid to form methyl 2,3,6-trideoxy-β-D-*glycero*-hexopyranosid-4-ulose (**23**, 72%), while **9** experienced ring contraction involving the pyranoid ring oxygen to form methyl 3,5-anhydro-2,6-dideoxy-β-D-*xylo*-hexofuranoside (**20**, 54%). Compound **11** produced methyl 3-*C*-aldehydo-2,5-dideoxy-β-D-*threo*-pentofuranoside (**13**, 65%). Upon reaction with triflic anhydride, methyl 2,6-dideoxy-β-D-*arabino*- and -*xylo*-hexopyranosides (**5** and **6**, respectively) generated hydroxy triflates which were not isolated due to their further reaction below room temperature. Compound **5** produced aldehyde **13** (54%) while reaction of **6** gave methyl 3,4-anhydro-2,6-dideoxy-β-D-*lyxo*- and -*ribo*-hexopyranosides [**15** (48%) and **16** (24%), respectively]. The mechanisms for these reactions are discussed and the reactivity of the hydroxy triflates is compared to that of related carbohydrate derivatives.

Compounds with neighboring hydroxyl and triflyloxy groups should be among the most reactive of all carbohydrate derivatives since these materials potentially are capable of intramolecular triflate (trifluoromethanesulfonate) displacement leading to anhydro sugars and ring-contraction products (Scheme I, paths a and b). The only reaction in the carbohydrate literature which directly supports the anticipated reactivity of hydroxy triflates is the spontaneous cyclization of compound **1** (eq 1).[1] In what initially appears to be an additional supportive example, the triflate **2** undergoes a ring-contraction reaction (eq 2); however, this process is not truly indicative of unusual triflate reactivity since strongly basic, reducing conditions (sodium in liquid ammonia) are required for reaction.[2] The remaining vicinal, hydroxy triflates which have been studied undergo normal displacement[3-5] or hydroxyl group derivitization[6] reactions, although formation of unidentified products has been noted.[7,8]




(eq. 1)

**1**

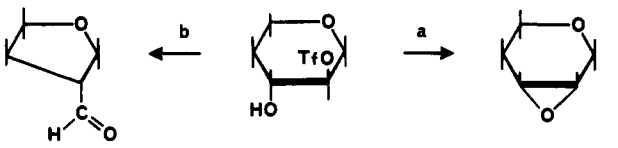



(eq. 2)

**2**

Since the available information about hydroxy triflates leaves unclear the type of reactivity that generally should be expected from these compounds and since this uncertainty, at least in part, is a result of the considerable difference in the structures of the compounds studied,[1-8] an investigation of a group of related hydroxy triflates seemed worthwhile. Such a study should involve compounds with similar structures which contain only the hydroxyl and triflyloxy functional groups; also, these compounds should include the basic types of stereochemical relationships possible between the two groups. Hydroxy triflates derived from the readily available 2,6-dideoxy sugars **3–6** (Table I) should provide the necessary compounds for such a study.

Scheme I




## Results and Discussion

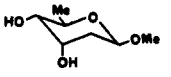
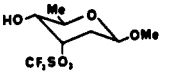
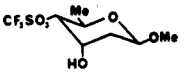
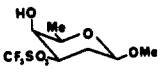
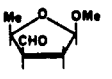
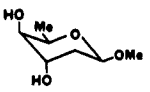
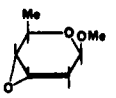
The synthesis of the desired triflates was undertaken by treatment of the dideoxy sugars **3–6** with equal molar amounts of triflic anhydride in methylene chloride in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (**7**). (Pyridine itself was not used as a base since it is sufficiently nucleophilic to cause displacement in some reactive triflates.) These reactions gave the products shown in Table I. Hydroxy triflates **8**, **9**, and **11** were obtained in 15, 73, and 84% yields, respectively, from the dideoxy sugars **3** and **4**; in contrast, reaction of compound **5** produced the ring-contraction product **13** (54%) while treatment of **6** (with triflic anhydride) gave the anhydro sugars **15** (48%) and **16** (21%), respectively.

Formation of compounds **13**, **15**, and **16** suggested that reaction of the dideoxy sugars **5** and **6** produced three additional hydroxy triflates (**17–19**), which were too reactive to be isolated. Since these triflates (**17–19**) (Table II) might have been detectable before chromatography, the $^{13}C$ NMR spectra of the crude mixtures from **5** and **6** were determined immediately after esterification; no resonances attributable to hydroxy triflates were observed. These results indicated that **17–19**, once formed, reacted rapidly at room temperature. Such behavior seemed reasonable for these compounds. Triflates **18** and **19** have the trans, diaxial arrangement of neighboring hydroxyl and triflyloxy groups desirable for rapid anhydro sugar formation.[9] Compound **17** also has a structure which favors intramo-

(1) Binkley, R. W. *J. Carbohydr. Chem.* **1985**, *4*, 227.
(2) Tsutomu, T.; Nakamura, F.; Umezawa, S. *Tetrahedron Lett.* **1979**, 2805.
(3) Haskell, T. H.; Woo, P. W. K.; Watson, D. R. *J. Org. Chem.* **1977**, *42*, 1302.
(4) Woo, P. W. K.; Haskell, T. H. *J. Antibiot.* **1982**, *35*, 692.
(5) Yasuda, N.; Matsuda, K.; Tsutsumi, H.; Takaya, T. *Chem. Lett.* **1984**, 1665. The displacement in this case is an internal one with the benzyloxycarbonyl group functioning as the nucleophile.
(6) Knapp, S.; Kukkoal, P. J.; Sharma, S.; Dhar, T. G. M.; Naughton, A. B. J. *J. Org. Chem.* **1990**, 5700.
(7) Liav, A.; Goren, M. B. *Carbohydr. Res.* **1983**, *123*, C22.
(8) Liav, A.; Goren, M. B. *Carbohydr. Res.* **1984**, *129*, 121.
(9) Since compounds **17–19** were too reactive to be observed directly, their conformations were assumed to be similar to those of closely related structures, e.g., the corresponding benzoates.[10]
(10) (a) Binkley, R. W. *J. Carbohydr. Chem.* **1990**, *9*, 771. (b) Binkley, R. W. *J. Org. Chem.* **1991**, *56*, 3892.

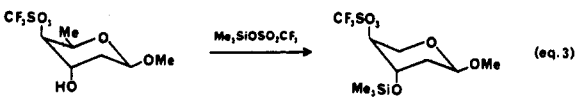
0022-3263/92/1957-2353$03.00/0 

**Table I. Reactions of Compounds 3–6 with Triflic Anhydride**

| starting material | 3-triflate | 4-triflate | other products | ditriflate |
|---|---|---|---|---|
|  3 |  8 (15 %) |  9 (73 %) | – | 10 (5%) |
|  4 |  11 (84 %) | – | – | – |
|  5 | – | – |  13 (54 %) | 12 (24%) |
|  6 | – | – |  15 (48 %)  16 (21 %) | 14 (17%) |

lecular reaction;[9] that is, the trans, coplanar arrangement of the C–O bond at $C_3$ and the $C_4$–$C_5$ ring bond has the proper stereochemistry for triflate departure with bond migration. Bond migration, when coupled with proton loss from $O_4$, would be assisted by the stabilizing effect of carbonyl group formation.

Since confirmation of the intermediacy of the unstable triflates 17–19 might be obtained by "trapping" these compounds before further reaction, the crude mixtures from treatment of compounds 5 and 6 with triflic anhydride were silylated[11] at –20 °C as soon as triflate formation was complete. The intramolecular reactions of 17 and 18 were too rapid for silylated triflates to be formed, but triflate 19 was sufficiently stable to be converted into the silyl triflate 24 (eq 3). None of the anhydro sugar 16 was produced under these conditions. This experiment provided additional support for the intermediacy of 19 in anhydro sugar formation.



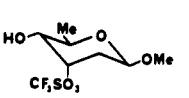
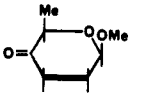
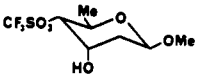
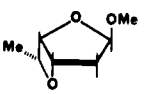
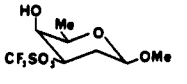
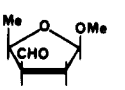
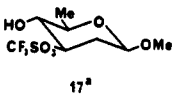
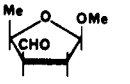
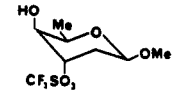
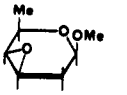
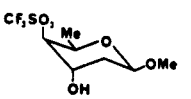
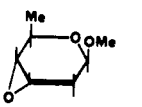

19 24 (eq. 3)

The triflates 9 and 11 were produced by regioselective esterification of equatorial hydroxyl groups. Knapp and co-workers[6] have observed that regioselective formation of monotriflates from vicinal diols correlates with the presence of a third substituent on the pyranoid ring which not only has an oxygen–carbon bond (e.g., a methoxy group) but also is both adjacent and cis related to the hydroxyl group experiencing preferential esterification. Since there is no appropriately placed substituent in compounds 3–6, regioselectivity of the type observed by the Knapp group would not be expected; consequently, the generally greater reactivity of equatorial hydroxyl groups[12] appears to be the controlling factor in the preferential formation of monotriflates 9 and 11.

(11) Trimethylsilyl triflate (Aldrich) was used as the "trapping agent" since it would introduce no nucleophiles which might lead to triflate displacement and since it is, even at –20 °C, a powerful silylating agent.

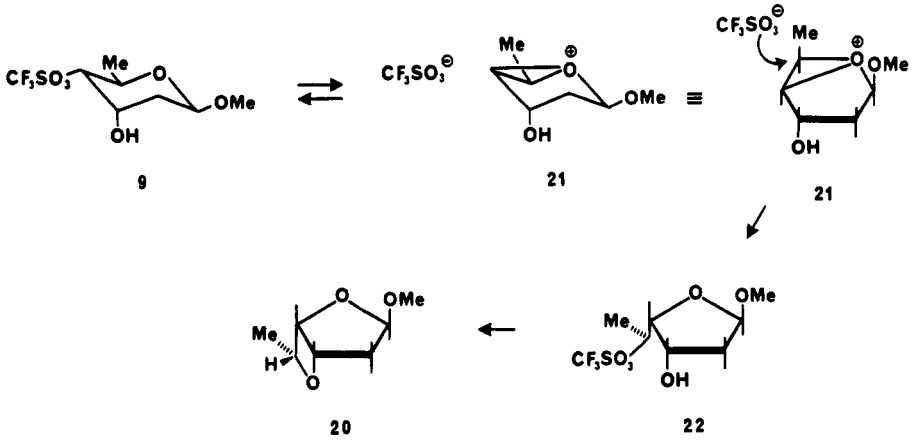
(12) Binkley, R. W. *Modern Carbohydrate Chemistry*; Marcel Dekker: New York, 1988; p 138.

**Table II. Reactions of Hydroxy Triflates**

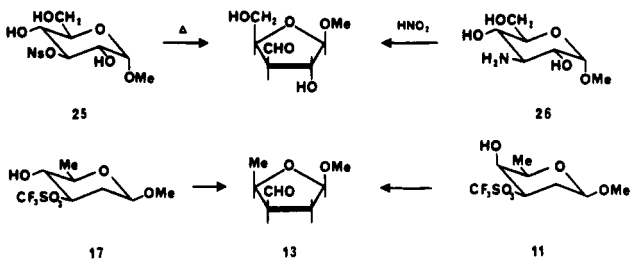
| triflate | product |
|---|---|
|  8 |  23 (72 %) |
|  9 |  20 (54 %) |
|  11 |  13 (65 %) |
|  17[a] |  13[b] |
|  18[a] |  15[b] |
|  19[a] |  16[b] |

[a] Too unstable for isolation. [b] Product yields in Table I.

**Scheme II**



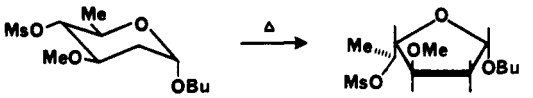
**Scheme III**



Although triflates 8, 9, and 11 could be isolated, they were not particularly stable. Compound 11 experienced ring contraction when heated at 80 °C in the presence of the hindered base 7 or at room temperature in pyridine to give 13 (Table II). (The stereochemistry at C-3 in 11, with the 4,5-bond in a trans coplaner relationship to the C–O bond at C-3, is well suited for ring contraction.) The hydroxy triflate 9 also had the proper stereochemistry for ring contraction but another process intervened. Heating 9 in the presence of 7 caused rearrangement to the bicyclic structure 20, a compound which is proposed (Scheme II) to result from participation of the ring oxygen in triflate displacement. Participation would generate the ion pair 21, an intermediate that can either re-form 9 or rearrange to the new triflate 22. Internal triflate displacement in 22 would produce 20. Finally, when compound 8 was heated in the presence of the hindered base 7, it lost the elements of triflic acid to form the ulose 23.

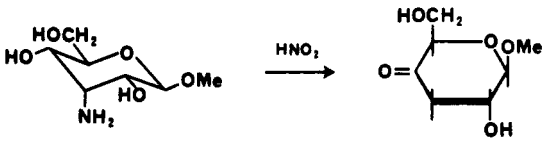
It is informative to compare the reactions of hydroxy triflates with those of other sulfonate esters and with nitrous acid deamination of aminodeoxy sugars. Internal displacement reactions (such as those experienced by 18 and 19) that produce anhydro sugars are common for sulfonate esters.[13] Ring contraction is known to occur for a number of these compounds, but the reactions observed for the hydroxy triflates 11 and 17 resemble most closely the rearrangement of the *p*-nitrobenzenesulfonate 25[14,15] (Scheme III). The primary difference is that the triflates react at (or below) room temperature while the *p*-nitrobenzenesulfonate (25) requires heating to 100 °C. With respect to ease of reaction, triflates parallel more closely nitrous acid deamination, which leads to room-temperature ring contraction for the aminodeoxy sugar 26.[14,15] (Scheme III).

Participation of the ring oxygen sometimes is observed in displacement reactions at the 4-position in pyranoid systems, particularly in those situations where substitution is difficult.[16] For example, refluxing the mesylate 27 in DMF causes ring contraction via ring-oxygen participation (eq 4).[17] This type of process, which occurs for other 4-*O*-sulfonyl-substituted compounds[18–20] as well as in deamination reactions[21] is analogous to that suggested in Scheme II for the hydroxy triflate 9. Finally, deamination of the 3-amino-3-deoxy sugar 28 produces a carbonyl compound (eq 5) similar to that formed by reaction of the



(eq. 4)

27



(eq. 5)

28

hydroxy triflate 8.[22] It is reasonable that reactions of these two compounds (8 and 28) should have similarity since both involve a reactive, axial leaving group but for neither is anhydro sugar formation possible.

A final observation concerns the general reactivity of hydroxy triflates. The difference in stability between the compounds reported here and their more stable counterparts described in the literature[2–8] appears to depend upon the presence of other functional groups. Since the early stages of the internal substitution and rearrangement reactions should create electron deficiency on the carbon atom bearing the leaving group, it is understandable to find that the hydroxy triflates mentioned in the literature, which have additional electron-withdrawing ring substituents when compared to the triflates described here, should have increased stability and consequently be less reactive.[23]

(13) Ball, D. H.; Parrish, F. W. *Adv. Carbohydr. Chem. Biochem.* **1969**, *24*, 167.
(14) Austin, P. W.; Buchanan, J. G.; Saunders, R. M. *J. Chem. Soc., Chem. Commun.* **1965**, 146; *J. Chem. Soc. C* **1967**, 372.
(15) Inoue, S.; Ogawa, H. *Chem. Pharm. Bull.* **1960**, *8*, 79.
(16) Hough, L.; Richardson, A. C. In *The Carbohydrates*; Pigman, W., Horton, D., Eds; Academic Press: New York, 1972; Vol. IA, p 141.
(17) Berti, G.; Catelani, G.; Colonna, F.; Ferretti, M.; Monti, L. *Gazz. Chim. Ital.* **1985**, *115*, 85.
(18) Stevens, C. L.; Glenski, R. D.; Taylor, G.; Blumbergs, P.; Sirokmann, F. *J. Am. Chem. Soc.* **1966**, *88*, 2073.
(19) Hanessian, S. *J. Chem. Soc., Chem. Commun.* **1966**, 196.
(20) Jary, J.; Novak, P.; Samek, Z. *Ann.* **1970**, *740*, 98.
(21) Ng Ying Kin, N. M. K.; Williams, J. M.; Horsington, A. *J. Chem. Soc C* **1971**, 1578; *J. Chem. Soc., Chem. Commun.* **1969**, 971.
(22) Ng Ying Kin, N. M. K.; Williams, J. M. *J. Chem. Soc., Chem. Commun.* **1971**, 1123.

## Experimental Section

**General Procedures.** $^1H$ NMR (300 MHz) and $^{13}C$ NMR (75 MHz) spectra were determined in $CDCl_3$. Column chromatography was conducted using a 2.5- × 15-cm column of 240–400-mesh silica gel with hexane–ethyl acetate (3:1) as the developer. TLC was done using silica gel plates developed with hexane–ethyl acetate (9:1), unless otherwise noted. Optical rotations were determined at 578 nm for solutions in ethyl acetate at 22 °C.

**General Procedure for Triflate Synthesis.** To the sugar (3.0 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (7, 7.0 mmol) in 15 mL of anhydrous methylene chloride at −20 °C was added 3.3 mmol of triflic anhydride in 3 mL of methylene chloride. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature over a period of 30 min. Saturated aqueous sodium bicarbonate solution (10 mL) was added to the rapidly stirred reaction mixture. The phases were separated, and the aqueous phase was extracted with 2 × 20 mL of methylene chloride. The solvent was distilled from the combined organic extracts, and the residue was chromatographed in the standard fashion. Those hydroxy triflates which could be isolated all began to decompose within a few hours upon standing at room temperature.

**Methyl 2,6-Dideoxy-4-*O*-[(trifluoromethyl)sulfonyl]-β-D-*ribo*-hexopyranoside (9) and Methyl 2,6-Dideoxy-3-*O*-[(trifluoromethyl)sulfonyl]-β-D-*ribo*-hexopyranoside (8).** Reaction of methyl 2,6-dideoxy-β-D-*ribo*-hexopyranoside (3) according to the standard synthesis and isolation procedure produced compound **9** in 73% yield: $R_f$ 0.14; $[\alpha] = +35°$ ($c = 0.69$); $^1H$ NMR δ 1.36 ($H_6$, $J_{5,6} = 6.4$ Hz), 1.83 ($H_{2a}$, $J_{1,2a} = 8.9$ Hz, $J_{2a,3} = 3.0$ Hz, $J_{2a,2e} = 14.0$ Hz), 2.18 ($H_{2e}$, $J_{1,2e} = 2.3$ Hz, $J_{2e,3} = 4.5$ Hz), 3.49 (OMe), 4.18 ($H_5$, $J_{4,5} = 8.9$ Hz), 4.43 ($H_3$, $J_{3,4} = 2.7$ Hz), 4.58 ($H_4$), 4.81 ($H_1$); $^{13}C$ NMR δ 17.69 ($C_6$), 37.66, 56.70 (OMe), 66.16 ($C_3$), 66.67 ($C_5$), 89.09 ($C_4$), 98.66 ($C_1$), 118.40 ($CF_3$). Also formed was methyl 2,6-dideoxy-3-*O*-[(trifluoromethyl)-sulfonyl]-β-D-*ribo*-hexopyranoside (8). NMR spectra of the crude reaction mixture indicated **8** to be present in about 15% yield; however, it decomposed on the chromatography column sufficiently rapidly that it was isolated in only 3% yield: $R_f$ 0.12; $^1H$ NMR δ 1.37 ($H_6$, $J_{5,6} = 6.2$ Hz), 1.95 ($H_{2a}$, $J_{1,2a} = 9.2$ Hz, $J_{2a,3} = 2.8$ Hz, $J_{2a,2e} = 14.0$ Hz), 2.34 ($H_{2e}$, $J_{1,2e} = 2.0$ Hz, $J_{2e,3} = 3.8$ Hz), 3.51 (OMe), 3.79 ($H_5$, $J_{4,5} = 9.1$ Hz), 5.29 ($H_3$, $J_{3,4} = 3.4$ Hz), 3.53 ($H_4$), 4.69 ($H_1$); $^{13}C$ NMR δ 17.89 ($C_6$), 36.26 ($C_2$), 56.66 (OMe), 87.22 ($C_3$), 69.74 ($C_5$), 70.98 ($C_4$), 97.90 ($C_1$), 118.40 ($CF_3$). Compounds **8** and **9** were not sufficiently stable for elemental analysis. Finally, a small amount (5%) of methyl 2,6-dideoxy-3,4-bis-*O*-[(trifluoromethyl)sulfonyl]-β-D-*ribo*-hexopyranoside (**10**), identical with a previously prepared sample,[25] was isolated.

**Methyl 2,6-Dideoxy-3-*O*-[(trifluoromethyl)sulfonyl]-β-D-*lyxo*-hexopyranoside (11).** Reaction of methyl 2,6-dideoxy-β-D-*lyxo*-hexopyranoside (4) by the standard procedures gave compound **11** in 84% yield: $R_f$ 0.15; $[\alpha] = -3.5°$ ($c = 0.34$); $^1H$ NMR δ 1.76 ($H_6$, $J_{5,6} = 6.4$ Hz), 2.13 ($H_{2a}$, $J_{1,2a} = 9.1$ Hz, $J_{2a,3} = 11.9$ Hz, $J_{2a,2e} = 12.3$ Hz), 2.32 ($H_{2e}$, $J_{1,2e} = 2.7$ Hz, $J_{2e,3} = 5.7$ Hz), 3.51 (OMe), 3.53 ($H_5$, $J_{4,5} < 1$ Hz), 4.91 ($H_3$, $J_{3,4} = 2.9$ Hz), 3.83 ($H_4$), 4.40 ($H_1$); $^{13}C$ NMR δ 16.38 ($C_6$), 32.01 ($C_2$), 56.85 (OMe), 85.70 ($C_3$), 66.80 ($C_5$), 69.86 ($C_4$), 100.26 ($C_1$), 118.40 ($CF_3$). This compound was not sufficiently stable for elemental analysis.

**Reaction of Methyl 2,6-Dideoxy-β-D-*arabino*-hexopyranoside (5) with Triflic Anhydride.** Reaction of methyl 2,6-dideoxy-β-D-*arabino*-hexopyranoside (5) with triflic anhydride according to the standard procedure for triflate formation gave methyl 3-*C*-aldehydo-2,5-dideoxy-β-D-*threo*-pentofuranoside (**13**) in 54% yield: $R_f$ 0.17; $[\alpha] = -6.5°$ ($c = 0.94$); $^1H$ NMR (pyridine-$d_5$) δ 1.26 ($H_5$, $J_{4,5} = 6.7$ Hz), 2.10 ($H_{2'}$, $J_{1,2'} = 9.0$ Hz, $J_{2',3} = 5.4$ Hz, $J_{2,2'} = 13.6$ Hz), 2.33 ($H_2$, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 4.0$ Hz), 3.25 (OMe), 2.88 ($H_3$, $J_{3,4} = 6.9$ Hz), 4.39 ($H_4$), 4.98 ($H_1$), CHO ($J_{CHO,3} = 3.9$ Hz); $^{13}C$ NMR δ 18.38 ($C_5$), 34.30 ($C_2$), 52.74 ($C_3$), 54.71 (OMe), 76.95 ($C_4$), 105.03 ($C_1$), 202.98 (CHO). Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.00; H, 8.44. Also isolated in 24% yield was methyl 2,6-dideoxy-3,4-bis-*O*-[(trifluoromethyl)-sulfonyl]-β-D-*arabino*-hexopyranoside (**12**), identical to a previously prepared sample.[25]

**Reaction of Methyl 2,6-Dideoxy-β-D-*xylo*-hexopyranoside (6) with Triflic Anhydride.** Reaction of methyl 2,6-dideoxy-β-D-*xylo*-hexopyranoside (6) according to the standard synthesis and isolation procedure produced methyl 3,4-anhydro-2,6-dideoxy-β-D-*lyxo*-hexopyranoside (**15**) in 48% yield: $R_f$ 0.14; $[\alpha] = -98°$ ($c = 1.10$); $^1H$ NMR δ 1.41 ($H_6$, $J_{5,6} = 6.5$ Hz), 1.90 ($H_{2a}$, $J_{1,2a} = 9.2$ Hz, $J_{2a,3} < 1$ Hz, $J_{2a,2e} = 15.2$ Hz), 2.07 ($H_{2e}$, $J_{1,2e} = 3.9$ Hz, $J_{2e,3} = 5.4$ Hz), 3.43 (OMe), 3.98 ($H_5$), 3.27 ($H_3$, $J_{3,4} = 3.9$ Hz), 2.92 ($H_4$), 4.31 ($H_1$); $^{13}C$ NMR δ 17.86 ($C_6$), 29.30 ($C_2$), 55.94 (OMe), 49.77 ($C_3$), 68.28 ($C_5$), 52.47 ($C_4$), 99.72 ($C_1$). This compound had a $^1H$ NMR spectrum identical to that reported in the literature.[26] Also formed was methyl 3,4-anhydro-2,6-dideoxy-β-D-*ribo*-hexopyranoside (**16**): $R_f$ 0.12; $[\alpha] = -56°$ ($c = 1.10$); $^1H$ NMR δ 1.34 ($H_6$, $J_{5,6} = 6.9$ Hz), 1.74 ($H_{2a}$, $J_{1,2a} = 8.9$ Hz, $J_{2a,3} = 2.1$ Hz, $J_{2a,2e} = 14.4$ Hz), 2.21 ($H_{2e}$, $J_{1,2e} = 2.9$ Hz, $J_{2e,3} = 2.2$ Hz), 3.38 (OMe), 4.00 ($H_5$), 3.33 ($H_3$, $J_{3,4} = 4.1$ Hz), 2.93 ($H_4$), 4.36 ($H_1$); $^{13}C$ NMR δ 19.30 ($C_6$), 31.16, 56.48 (OMe), 53.04 ($C_3$), 70.74 ($C_5$), 55.03 ($C_4$), 98.20 ($C_1$). This compound had a $^1H$ NMR spectrum identical to that reported in the literature.[26] Finally, a small amount (17%) of methyl 2,6-dideoxy-3,4-bis-*O*-[(trifluoromethyl)sulfonyl]-β-D-*xylo*-hexopyranoside (**14**), identical in NMR spectra with a previously prepared sample,[25] was isolated.

**Thermal Reactions of Compounds 8, 9, and 11.** The following general procedure was used. The triflate (180 mg, 0.62 mmol) was combined with 480 mg (2.3 mmol) of the hindered base **7** in 2 mL of benzene, and the reaction mixture was heated at 80 °C for 30 min. The solvent then was removed under reduced pressure, and the reaction mixture was chromatographed in the standard fashion.

**A. Compound 11.** Reaction under the standard conditions of the triflate **11** gave the aldehyde **13** (65%), which was identical to the aldehyde produced from reaction of **5**.

**B. Compound 9.** After reaction and product isolation according to the standard procedure, the triflate **9** gave methyl 3,5-anhydro-2,6-dideoxy-β-D-*xylo*-hexofuranoside (**20**) in 54% yield. (This compound is relatively volatile; consequently, some material was certainly lost during the isolation procedure.) Characterizing data for **20**: $[\alpha] = -22°$ ($c = 0.17$); $R_f$ 0.11; $^1H$ NMR δ 1.26 ($H_6$, $J_{5,6} = 6.1$ Hz), 1.88 ($H_2$, $J_{1,2} = 4.3$ Hz, $J_{2,3} = 5.7$ Hz), 2.37 ($H_{2'}$, $J_{1,2'} = 5.2$ Hz, $J_{2',3} = 1.1$ Hz), 3.46 (OMe), 4.8–4.9 ($H_4$, $H_5$) 5.26 ($H_3$, $J_{3,4} = 3.7$ Hz), 5.45 ($H_1$); $^{13}C$ NMR δ 15.91 ($C_6$), 40.90 ($C_2$), 56.12 (OMe), 79.20, 80.52, 81.86 ($C_3$, $C_4$, $C_5$), 108.88 ($C_1$). Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.23; H, 8.58.

**C. Compound 8.** Upon thermal reaction under the standard conditions, the triflate **8** gave methyl 2,3,6-trideoxy-β-D-*glycero*-hexopyranosid-4-ulose (**23**) (72%): $[\alpha] = -56°$ ($c = 1.01$); $R_f$ 0.15, $^1H$ NMR δ 1.39 ($H_6$, $J_{5,6} = 6.9$ Hz), 2.09 ($H_{2'}$, $J_{1,2'} = 6.2$ Hz, $J_{2',3} = 8.5$ Hz, $J_{2',2} = 13.9$ Hz, $J_{2',3'} = 6.5$ Hz), 2.22 ($H_2$, $J_{1,2} = 3.6$ Hz, $J_{2,3} = 6.5$ Hz, $J_{2,3'} = 6.5$ Hz), 2.43 ($H_{3'}$, $J_{3,3'} = 16.5$ Hz), 2.65 ($H_{3'}$), 3.50 (OMe), 4.00 ($H_5$), 4.84 ($H_1$); $^{13}C$ NMR δ 17.04 ($C_6$), 33.78, 55.93 (OMe), 29.56 ($C_3$), 76.20 ($C_5$), 99.64 ($C_1$). Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.11; H, 8.35.

**Trimethylsilylation of Compound 9.** The procedure for triflate synthesis for compound **6** was followed except that trimethylsilyl triflate[11] was added, after the starting material had completely reacted (TLC) but before the reaction mixture was allowed to warm to room temperature. Under these conditions compound **18** was still formed but **19** was not. A new product methyl 4-*O*-[(trifluoromethyl)sulfonyl]-3-*O*-(trimethylsilyl)-β-D-*xylo*-hexopyranoside (**24**) was produced in 13% yield: $R_f$ 0.20; $[\alpha] = +5.7°$ ($c = 0.33$); $^1H$ NMR δ 1.34 ($H_6$, $J_{5,6} = 6.6$ Hz), 1.86 ($H_{2a}$, $J_{1,2a} = 8.4$ Hz, $J_{2a,3} = 3.0$ Hz, $J_{2a,2e} = 14.6$ Hz), 1.78 ($H_{2e}$, $J_{1,2e} = 3.3$ Hz, $J_{2e,3} = 2.6$ Hz), 3.50 (OMe), 4.19 ($H_5$, $J_{4,5} = 0.8$ Hz), 4.25 ($H_3$, $J_{3,4} = 3.4$ Hz), 4.35 ($H_4$), 4.70 ($H_1$); $^{13}C$ NMR δ 16.48 ($C_6$), 33.98 ($C_2$), 56.35 (OMe), 67.43 ($C_3$), 66.87 ($C_5$), 85.06 ($C_4$), 98.89 ($C_1$).

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(23) The presence of electron-withdrawing substituents has been shown to stabilize simple organic triflates.[24]

(24) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673.

(25) Binkley, R. W. *J. Carbohydr. Chem.*, in press.

(26) Martin, A.; Pais, M.; Monneret, C. *Carbohydr. Res.* **1983**, *113*, 189.