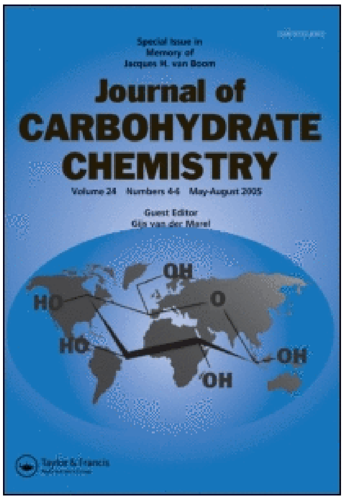

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Displacement Reactions OP vicinal ditriflates

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COMMUNICATION

DISPLACEMENT REACTIONS OF VICINAL DITRIFLATES

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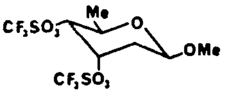
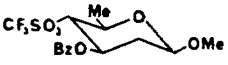
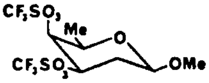
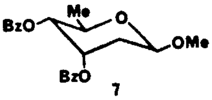
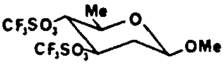
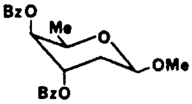
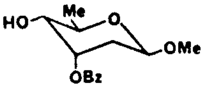
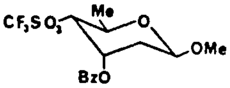
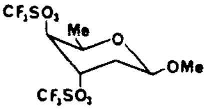
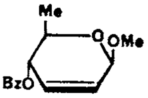
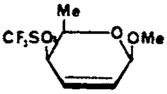
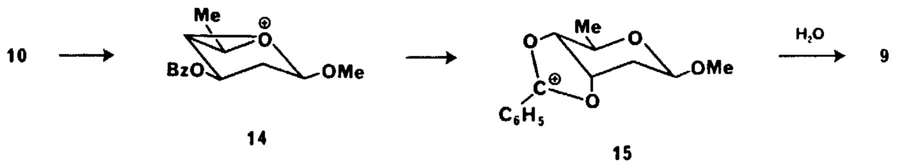
Although trifluoromethanesulfonate (triflate) displacement from carbohydrates has become a common synthetic reaction, instances in which two triflyloxy groups are replaced in the same molecule are relatively rare. In most of the ditriflates studied, the triflyloxy groups actually are remote from each other (e.g., in different rings of a disaccharide[1-4] or on non-neighboring carbon atoms[5-8]) and, as might be expected, the reactivity of these molecules is fundamentally the same as that of monotriflates. Even for those compounds where the two triflyloxy groups are adjacent to each other, the only reactions which have been observed are those which involve direct displacement[9] or the Tipson-Cohen reaction.[10,11] Since it seemed possible that other reactions (e.g., ring contraction, internal displacement) might occur for vicinal ditriflates, a study was undertaken of a group of simple, conformationally flexible compounds (**1-4**) with neighboring triflyloxy groups.

It was necessary to conduct ditriflate synthesis at a lower temperature (-50 °C) than that typically used for monotriflates[12] (-10 °C) in order to obtain optimum yields. In a typical reaction, 0.20 g of methyl 2,6-dideoxy-ß-D-hexopyranoside was dissolved in 15 mL of dichloromethane which contained 1.0 mL of pyridine. This solution was

TABLE I. REACTIONS OF DITRIFLATES 1-4 WITH TETRABUTYLAMMONIUM BENZOATE

STARTING MATERIAL	DIBENZOATE	OTHER PRODUCT	INTERMEDIATE
 1	NONE	 5 81 %	 6
 2	 7 89 %	NONE	NONE
 3	 8 63 %	 9 22 %	 10
 4	 11 26 %	 12 64 %	 13



Scheme I

stirred and cooled to -50 ^{0}C (dry ice - acetonitrile) and a solution of 1.4 g of triflic anhydride was added in a dropwise manner. The reaction mixture was held at -50 ^{0}C for 90 min and then allowed to warm to room temperature over a period of one h. The solvent was removed under reduced pressure and the residue chromatographed to give the ditriflates **1-4**,[13] compounds which began to decompose when left at room temperature for more than a few h and, therefore, were used immediately after isolation.

Each ditriflate (0.20), after dissolving in a mixture of 10 mL of toluene and 1 mL of water containing 0.50 g of tetrabutylammonium benzoate, was stirred for 24 h at room temperature. Compounds **1** and **4** reacted under these conditions but for **2** and **3** heating under reflux for one h was required. The solvent then was distilled and the residue was chromatographed to give the products shown in Table I.[14]

Although direct double displacement to produce dibenzoates does occur for three (**2-4**) of the four ditriflates, reactions other than simple substitution also are important. For compounds **1** and **3** these "other" reactions occur because a second triflyloxy group still is present in the molecule following the initial displacement process. Thus, reaction of **1** produces the monotriflate **6**, which can experience internal displacement by the benzoyloxy group to give **5**.[15] (Compound **6** was detected in the reaction mixture during treatment of **1** with tetrabutylammonium benzoate and, in a separate experiment, was shown to produce **5** under the reaction conditions.) In a similar manner, monotriflate **10** was shown to be an intermediate in the formation **9**. (Subjecting **10** to the reaction conditions produced **9** as well as the dibenzoate **8**.) A competition exists between direct displacement by benzoate from the monotriflate **10** (to give **8**) and internal substitution involving the ring oxygen (to afford **9**) (Scheme 1). Internal displacement of the 4-O-triflyloxy group in **10** by the ring oxygen leads to the intermediate **15**, a cation that has been shown to be involved in the formation of **9**.[15,16] Additionally, compound **12** was found to be formed from the ditriflate **4** via the intermediate monotriflate **13**. In the reaction of **4**, elimination competes effectively with substitution because the axial triflyloxy groups at C-3 and C-4 in the ditriflate **4** make difficult the approach of a nucleophile to either of these carbon atoms. As a final observation, it is worth noting that the reactions of compounds **1-4** provide additional examples supporting the observation that axial triflyloxy groups are displaced more easily than equatorial ones.[16]

In summary, the products from reactions of compounds **1-4** with tetrabutylammonium benzoate provide clear evidence that processes other than simple displacement can be expected when vicinal ditriflates react with nucleophiles. Although no reactions were observed which could be attributed to a unique interaction between neighboring triflyloxy groups, such processes may appear in our continuing studies of the chemistry of these unusual compounds.

ACKNOWLEDGMENT

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13. Characterizing data for compounds **1-4** [R_f values were determined in 9:1 (hexane: ethyl acetate), rotations were run in ethyl acetate, and NMR spectra were determined in $CDCl_3$]: Methyl 2,6-dideoxy-3,4-di-*O*-[(trifluoromethyl)sulfonyl]-β-D-*ribo*-hexopyranoside (**1**), [α] = +1.7^0 (c = 1.14); R_f = 0.33. ^1H NMR: δ 1.42 (H_6, $J_{5,6}$ = 6.4 Hz), 2.45 (H_{2e}, $J_{1,2e}$ = 2.2 Hz, $J_{2e,2a}$ = 14.8 Hz, $J_{2e,3}$ = 5.1 Hz), 2.08 (H_{2a}, $J_{1,2a}$ = 8.3 Hz, $J_{2a,3}$ = 2.7 Hz), 4.17 (H_5, $J_{4,5}$ = 8.4 Hz), 3.50 (OMe), 4.79 (H_1), 5.47 (H_3, $J_{3,4}$ = 2.4 Hz), 4.67 (H_4). ^{13}C NMR: δ 17.39 (C_6), 36.10 (C_2), 56.48 (OMe), 67.77 (C_5), 83.21 (C_4), 81.97 (C_3), 97.76 (C_1), 118.17 (CF_3, $J_{C,F}$ = 317 Hz). Methyl 2,6-dideoxy-3,4-di-*O*-[(trifluoromethyl)-

sulfonyl]-ß-D-lyxo-hexopyranoside (**2**), [α] = +76^0 (c = 0.58); R_f = 0.15. ^{1}H NMR: δ 1.44 (H_6, $J_{5,6}$ = 6.5 Hz), 2.32 (H_{2e}, $J_{1,2e}$ = 2.2 Hz, $J_{2e,2a}$ = 12.4 Hz, $J_{2e,3}$ = 5.3 Hz), 2.13 (H_{2a}, $J_{1,2a}$ = 9.5 Hz, $J_{2a,3}$ = 12.4 Hz), 3.75 (H_5, $J_{4,5}$ < 1 Hz), 3.53 (OMe), 4.48 (H_1), 5.05 (H_3, $J_{3,4}$ = 9.2 Hz), 5.02 (H_4). ^{13}C NMR: δ 16.50 (C_6), 32.38 (C_2), 56.81 (OMe), 68.24 (C_5), 82.19 (C_4), 80.44 (C_3), 99.50 (C_1), 118.99 (CF_3, $J_{C,F}$ = 317 Hz). Methyl 2,6-dideoxy-3,4-di-O-[(trifluoromethyl)sulfonyl]-ß-D-arabino-hexopyranoside (**3**), [α] = +24^0 (c = 0.53); R_f = 0.25. ^{1}H NMR: δ 1.48 (H_6, $J_{5,6}$ = 6.2 Hz), 2.68 (H_{2e}, $J_{1,2e}$ = 2.0 Hz, $J_{2e,2a}$ = 12.3 Hz, $J_{2e,3}$ = 5.6 Hz), 2.05 (H_{2a}, $J_{1,2a}$ = 9.5 Hz, $J_{2a,3}$ = 12.2 Hz), 3.64 (H_5, $J_{4,5}$ = 9.2 Hz), 3.51 (OMe), 4.49 (H_1), 5.03 (H_3, $J_{3,4}$ = 9.2 Hz), 4.62 (H_4). ^{13}C NMR: δ 17.48 (C_6), 37.41 (C_2), 56.90 (OMe), 69.08 (C_5), 84.61 (C_4), 81.95 (C_3), 99.02 (C_1), 118.99 (CF_3, $J_{C,F}$ = 317 Hz). Methyl 2,6-dideoxy-3,4-di-O-[(trifluoromethyl)sulfonyl]-ß-D-xylo-hexopyranoside (**4**), [α] = +15^0 (c = 0.10); R_f = 0.15. ^{1}H NMR (C_5D_5N): δ 1.42 (H_6, $J_{5,6}$ = 6.5 Hz), 2.31 (H_{2e}, $J_{1,2e}$ = 2.6 Hz, $J_{2e,2a}$ = 15.3 Hz, $J_{2e,3}$ = 3.1 Hz), 2.20 (H_{2a}, $J_{1,2a}$ = 8.5 Hz, $J_{2a,3}$ = 3.4 Hz), 3.34 (OMe), 4.24 (H_5), 4.71 (H_1), 5.73 (H_3, $J_{3,4}$ = 3.8 Hz), 5.39 (H_4). ^{13}C NMR: δ 16.00 (C_6), 32.16 (C_2), 56.39 (OMe), 67.37 (C_5), 79.48 (C_4), 80.90 (C_3), 97.60 (C_1), 118.99 (CF_3, $J_{C,F}$ = 317 Hz).

14. The products from reactions of the ditriflates **1-4** were found to be identical in ^{1}H and ^{13}C NMR spectra to compounds prepared in previous studies. References to the orginal preparations of these compounds are as follows: **5, 6** (R. W. Binkley, J. Carbohydr. Chem., **10**, in press); **9, 10** (referecnce 15); **8, 11** (R. W. Binkley, J. Org. Chem., **56**, in press). Characterizing data for **12** (a new compound): R_f = 0.47 (3:1 hexane: ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.39 (H_6, $J_{5,6}$ = 6.7 Hz), 6.02 (H_2, $J_{1,2}$ = 1.4 Hz, $J_{2,3}$ = 10.3 Hz), 3.50 (OMe), 4.01 (H_5, $J_{4,5}$ = 6.7 Hz), 5.13 (H_1), 5.95 (H_3, $J_{3,4}$ = 0.6 Hz), 5.36 (H_4). ^{13}C NMR: δ 18.02 (C_6), 130.33 (C_2), 54.98 (OMe), 70.18 (C_5), 71.45 (C_4), 128.28 (C_3), 97.06 (C_1). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 68.01; H, 6.61.

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