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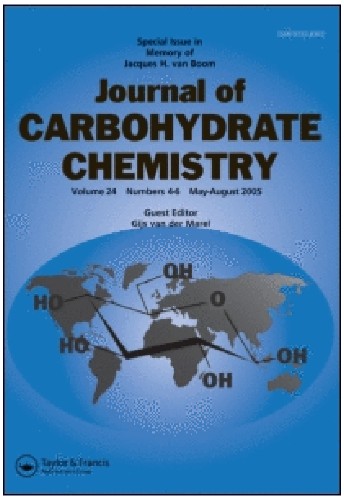

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COMMUNICATION

RING-OPENING OF A CARBOHYDRATE TRIFLATE TO FORM AN ACYCLIC ALKENE

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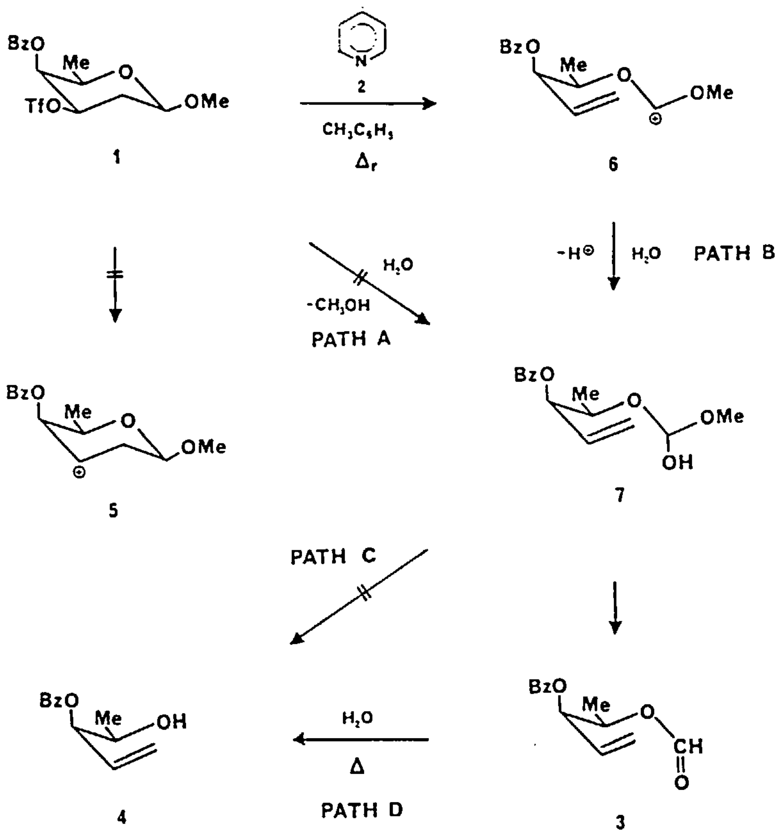
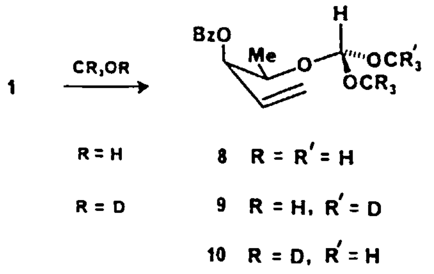
The ease with which carbohydrate trifluoromethanesulfonates (triflates) undergo substitution reactions with a wide variety of nucleophiles[1] has allowed these compounds to play an increasingly important role in synthetic carbohydrate chemistry.[2] The exceptional reactivity of triflates also creates an opportunity for unusual reactions to occur;[3] for example, triflyl group migration[4] and internal displacement by very weak nucleophiles[5] both have been observed. Also, carbohydrate triflates have been used as alkylating agents in oligosaccharide synthesis.[6] In this communication a new triflate reaction is described. This new process is one in which departure of the triflyloxy group is accompanied by ring opening to give an acyclic alkene.

When methyl 4-*O*-benzoyl-2,6-dideoxy-3-*O*-triflyl-β-D-*lyxo*-hexopyranoside (1)[7] (0.63 g, 1.58 mmol) was heated for 45 min under reflux in a solution consisting of toluene (5 mL), pyridine (5 mL) and water (1 mL), the two esters 3 and 4 of 4-penten-2,3-diol were formed in 47% and 40% yields, respectively.[8] The structures of these products suggested that a reaction was occurring in which there was simultaneous loss of the triflyloxy group and opening of the pyranoid ring (Scheme I). (Although triflate departure before ring opening was an *a priori* possibility, such a reaction was rendered unlikely by the absence of products arising from capture of the cyclic cation 5.[9]) It was not clear, however, whether water was partic-



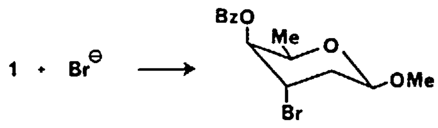
Scheme I

ipating in the process during ring-opening (Scheme I, path A) or simply was reacting with the cation 6 after its formation (path B). One way to choose between these possibilities, required the formation of a stable compound, such as an orthoester, analogous to the proposed intermediate 7; in fact, the orthoester 8 did form in 86% yield when methanol replaced water in the reaction of 1.[10] If formation of 8 were occurring in a concerted fashion, reaction of 1 with an alcohol other than methanol should produce a single orthoester rather than the pair of diastereomers expected from the intermediacy of 6. When such a reaction was conducted using CD_3OD, a mixture of the diastereomeric orthoesters 9 and 10 was produced.[10] This result supported the stepwise pathway B.



A remaining uncertainty about the mechanism of this reaction concerned the formation of the benzoate ester 4. Compound 4 could be produced either directly from 7 (Scheme I, path C) or by hydrolysis of 3 (path D). Since 7 also is a probable intermediate in hydrolysis of 8 and since orthoesters are easily hydrolyzed, it was possible to generate 7 and observe its reaction under conditions which did not permit the hydrolysis of 3. Under these conditions (moist silica gel and room temperature) only compound 3 (no 4) was formed; therefore, 3 is the only primary product from reaction of the triflate 1 in the presence of water. (Not surprisingly, when 3 is heated in toluene and water, 4 is produced.)

A ring-opening reaction of the type described here, which is analogous to a Grob fragmentation,[11,12] is made possible by the absence of an effective nucleophile. This fact is apparent when reaction of 1 (0.30 g, 0.75 mmol) is conducted in the presence of 1.0 g (3.1 mmol) of tetrabutylammonium bromide in dichloromethane for one h at 25 °C, since under these conditions the simple displacement product 11 is the only compound formed (in 96% yield). The contrast between bromide ion and water in their reactions with 1 suggests that further examination of triflate reactivity in the absence of effective nucleophiles, conditions not normally employed, could reveal other new reactions for this valuable class of compounds.



11

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1. Some recent references to substitution reactions involving carbohydrate triflates (and the nucleophile used) are: (a) G. W. J. Fleet, N. G. Ramsden, and D. R. Witty, *Tetrahedron*, 45, 319 (1989) (azide);

(b) G. Tarara and D. Hoppe, *Synthesis*, 89 (1989) (acetate); (c) R. W. Binkley, M. G. Ambrose, and D. G. Hehemann, *J. Carbohydr. Chem.*, 6, 203 (1987) (halides); (d) H. J. G. Broxterman, J. J. Neefjes, G. A. van der Marel, H. L. Ploegh, and J. H. van Boom, *J. Carbohydr. Chem.*, 7, 593 (1988) (benzyl amine); (e) M. S. Shekhani and W. Voelter, *Chemiker-Zeitung*, 113, 1 (1989) (hydrogen sulfate); (f) M. Blanc-Muesser and H. Driguez, *J. Chem. Soc. Perkin Trans. I*, 3345 (1988) (thioacetate).

2. For a review of the reactions of carbohydrate triflates see: R. W. Binkley and M. G. Ambrose, *J. Carbohydr. Chem.*, 3, 1 (1984).

3. As with other sulfonate esters elimination and ring-contractions sometimes are observed. See reference 2, pages 30-39.

4. (a) K. W. Pankiewicz, B. Nawrot, K. A. Watanabe, *J. Org. Chem.*, 51, 1525 (1986); (b) B. Nawrot, K. W. Pankiewicz, R. A. Zepf, and K. A. Watanabe, *J. Carbohydr. Chem.*, 7, 95 (1988).

5. (a) W. Tegge and C. E. Ballou, *Proc. Natl. Acad. Sci. USA*, 86, 94 (1989); (b) K. W. Pankiewicz, E. Sochacka, M. M. Kabat, L. A. Ciszewski, and K. A. Watanabe, *J. Org. Chem.*,, 53, 3473 (1988); (c) R. W. Binkley and M. A. Abdulaziz, *J. Org. Chem.*, 52, 4713 (1987); (d) R. W. Binkley and M. R. Sivik, *J. Org. Chem.*, 51 , 2619 (1986).

6. R. R. Schmidt and A. Esswein, *Angew. Chem. Int. Ed. Engl.*, 27 1178 (1988) and references cited therein.

7. Compound 1 was prepared by reaction of methyl 4-*O*-benzoyl-2,6-dideoxy-*β*-D-*lyxo*-hexopyranoside[5d] with triflic anhydride according to standard procedures.[1c]

8. Characterizing data for compounds 1, 3 and 4: Compound 3: ^{1}H NMR: δ 1.33 (H_1, $J_{1,2}$ = 6.5 Hz), 5.35 (H_2, $J_{1,2}$ = 6.3 Hz, $J_{2,3}$ = 6.5 Hz), 5.36 (H_{5C}, $J_{3,5C}$ = 1.2 Hz, $J_{4,5C}$ = 10.5 Hz), 5.47 (H_{5T}, $J_{3,5T}$ = 10 Hz, $J_{4,5T}$ = 17.1 Hz), 5.57 (H_3, $J_{3,4}$ = 6.5 Hz), 5.87 (H_4), 7.40-7.59, 8.05-8.08 (aromatic protons); ^{13}C NMR: δ 16.33 (C_1), 70.22 (C_2), 76.00 (C_3), 119.88 (C_5), 132.12 (C_4), 128.49, 129.82, 133.24 (aromatic carbons), 160.25 (HC=O), 165.40 (ArC=O). Anal. calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found C, 66.88; H, 5.89. Compound 4: ^{1}H NMR: δ 1.27 (H_1, $J_{1,2}$ = 6.4 Hz), 4.01 (H_2, $J_{2,3}$ = 6.2 Hz), 5.34 (H_{5C}, $J_{3,5C}$ = 1.2 Hz, $J_{4,5C}$ = 10.6 Hz), 5.39 (H_3, $J_{3,4}$ = 6.2 Hz, 5.44 (H_{5T}, $J_{3,5T}$ = 1.3 Hz, $J_{4,5T}$ = 17.2 Hz), 5.93 (H_4), 7.41-7.63, 8.05-8.10 (aromatic protons); ^{13}C NMR: δ 18.80 (C_1), 68.98 (C_2), 79.16 (C_3), 119.14 (C_5), 133.06 (C_4), 128.46, 129.68, 130.04, 133.20 (aromatic carbons), 165.81 (C=O). Anal. calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found C, 69.98; H, 6.89. Compound 1: ^{1}H NMR: δ 1.08 (H_6, $J_{5,6}$ = 6.4 Hz), 2.10 (H_{2e}, $J_{1,2e}$ = 2.1 Hz, $J_{2e,2a}$ = 12.2 Hz, $J_{2e,3}$ = 5.1 Hz), 2.31 (H_{2a}, $J_{1,2a}$ = 9.4 Hz, $J_{2a,3}$ = 12.0 Hz), 2.94 (H_5, $J_{4,5}$ = 0.8 Hz), 3.31 (OMe), 3.84 (H_1), 4.89 (H_3, $J_{3,4}$ = 3.3 Hz). 5.51 (H_4). 6.95-7.17, 8.11-8.21 (aromatic protons). ^{13}C NMR: δ 16.37 (C_1), 33.54 (C_2), 56.10 (OMe), 68.87 (C_5), 69.05 (C_4), 83.48 (C_3), 99.83 (C_1), 118.99 (CF_3, J_{CF} = 118.99 Hz), 128.71, 130.12, 133.42 (aromatic carbons), 165.67 (C=O).

9. The other alternative, heterolytic C_1-C_2 bond cleavage prior to triflate departure, was not deemed to be a realistic possibility. If such a reaction could occur, C_1-C_2 fragmentation reactions would be a common rather than a rare reaction for pyranosides.

10. The ^{1}H NMR spectrum of the inseparable mixture of 9 and 10 exhibited methoxy resonances at δ 3.33 and 3.28. The 3.28 resonance was approximately twice as intense as that at 3.33. The ^{13}C NMR spectrum also exhibited methoxy resonances of unequal intensity at 51.54 and 50.97 δ. The spectra of these compounds was otherwise identical to that of compound 8. ^{1}H NMR: δ 1.27 (H_1, $J_{1,2}$ = 6.4 Hz), 3.28, 3.33 (OMe), 4.07 (H_2, $J_{2,3}$ = 6.7 Hz, 5.20 [C$\underline{H}$(OMe$_2$], 5.32 (H_{5C}, $J_{3,5C}$ = 1.2 Hz, $J_{4,5C}$ = 10.6 Hz), 5.42 (H_{5T}, $J_{3,5T}$ = 1.3 Hz, $J_{4,5T}$ = 17.3 Hz), 5.58 (H_3, $J_{3,4}$ = 6.5 Hz), 5.96 (H_4), 7.38-7.61, 8.04-8.13 (aromatic protons); ^{13}C NMR: δ 16.51 (C_1), 50.97, 51.53 (OMe), 71.43 (C_2), 76.79 (C_3), 113.74 [$\underline{C}$H(OMe)$_2$], 118.54 (C_5), 132.72 (C_4), 128.42, 129.67, 133.06 (aromatic carbons), 165.44 (C=O).

11. C. A. Grob and P. W. Schiess, *Angew. Chem., Int. Ed. Engl.,* 6, 1 (1967).

12. The Grob fragmentation has been observed previously in carbohydrate systems. See W. W. Zajac, Jr., P. Dampawan, and D. Ditrow, *J. Org. Chem.,* 51, 2617 (1986) and references cited therein.