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An efficient one step dihydroxylation of 1,2-glycals with oxone in acetone☆

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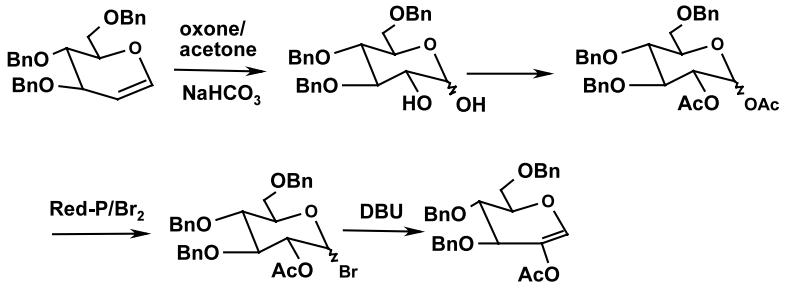
Abstract—A number of glycals have been converted into the corresponding 1,2-diols in fair to good yields. The reaction appears to proceed via the corresponding epoxide which opens in situ.

Differentially protected sugar 1,2-diols (Scheme 1) are useful intermediates in a variety of organic transformations. They are, for example, used in the synthesis of chiral polyols[2] and related natural products, in the synthesis of *O*-glycosides,[3] *C*-glycosides[4] and in intramolecular *O*-glycosylations as introduced by Hindsgaul,[5] Stork [6] and Bols.[7] One of the most commonly used methods[2,8] of preparing sugar derived 1,2-diols involves conversion of the corresponding acetobromosugars to *ortho* esters followed by hydrolysis. However, one of the drawbacks of this method is the necessity of using an excess of s-collidine as the solvent in the step leading to the formation of the *ortho* ester. Recently, OsO_4/NMO mediated dihydroxylation of 1,2-glycals has been reported[3a,c] as an alternative to the above method to obtain such 1,2-diols. In addition, hydrolytic opening of 1,2-glycal epoxides could be considered an alternative for the formation of 1,2-diols since glycal epoxides are now readily available by the epoxidation of glycals using dimethyl dioxirane.[9] While our work was in progress Danishefsky et al.[10] published on the formation of such diols using a similar strategy.

In connection with another project we had the opportunity to study the reactions of glycals with oxone in acetone without isolating dimethyl dioxirane and we have now found that in one step, 1,2-diols are obtained in fair to good yields. Five examples (Table 1) of differently protected glycals were studied and these gave moderate to good yields of the corresponding diols (almost a 1:1 anomeric mixture of the diols) which were characterised as their acetates.[11] It was found that the stereochemistry at C-2 is equatorial in every case. It is noteworthy that under these conditions acid labile acetonide protection survived (entry 4, Table 1). There is one report in the literature[12] where hydroxylation of olefins using oxone in strongly acidic aqueous medium is described. We therefore examined reactions of simple olefins with Oxone in acetone under the present conditions. Although the dihydroxylation did occur (Table



Scheme 1.

☆ Transformations in Carbohydrate Chemistry, Part 5. For Part 4, see Ref. 1.

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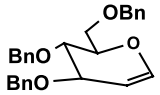
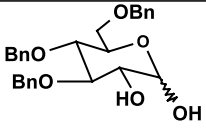
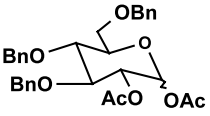
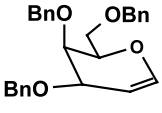
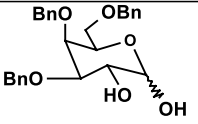
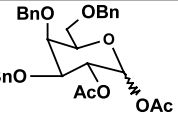
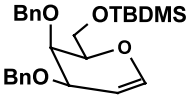
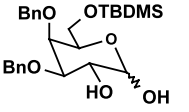
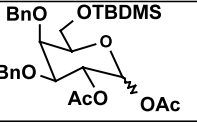
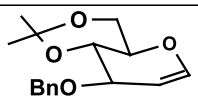
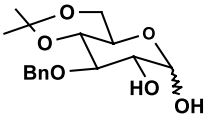
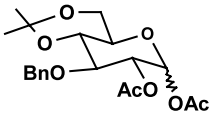
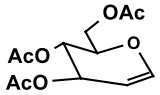
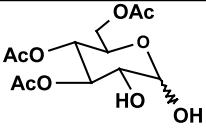
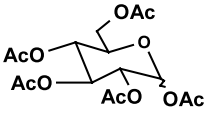
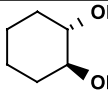
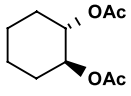
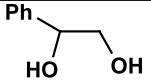
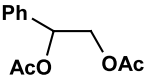
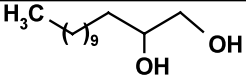
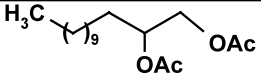
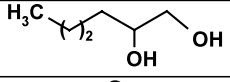
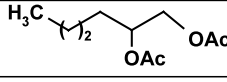
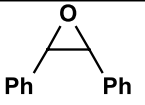
1), the conversion to products was generally low. The example using cyclohexene was chosen to assess the stereochemical outcome of the reaction. The corresponding diol was acetylated and the diacetate was found to be *trans* indicating clearly that the reaction proceeds via an epoxide.

Interestingly, among the non-carbohydrate substrates, cyclohexene gave a good yield of the diol, but stilbene gave an epoxide (entry 10, Table 1). In other cases the reaction was incomplete. It is clear that formation of epoxides and their subsequent opening is better with glycals as substrates. This is, however, not surprising since glycals are more nucleophilic than simple olefins and the corresponding epoxides are more reactive towards ring opening.

Lichtenthaler et al.[8a] in their pioneering work have shown that ulosyl bromides are useful intermediates in carboydrate chemistry. Typically, synthesis of ulosyl bromides involves bromination of the corresponding enol acetates which in turn are obtained from the corresponding *ortho* esters. In the present work, we converted a 1,2-diacetate into the corresponding bromoacetate (Scheme 1) using red P/Br_2 followed by elimination of the elements of HBr using DBU as a base to obtain the enol acetate. This enol acetate was readily converted into the ulosyl bromide by bromina-

Table 1. Dihydroxylation of 1,2-glycals and olefins using Oxone in acetone

S. No.	Glycals	1,2-diols	1,2-dicaetates	% yield[(i)]
1				81
2				74
3				53
4				47
5				73
6	cyclohexene			92
7	styrene			87[(ii)]
8	1-tridecene			88[(iii)]
9	1-hexene			90[(iv)]
10	*cis*-stilbene		—	98

(i) overall yield. (ii) based on 30% recovered starting material. (iii) based on 62% recovered starting material. (iv) based on 50% recovered starting material.

tion with NBS as reported by Lichtenthaler. The present sequence of reactions is, therefore, useful and offers a convenient alternative to the existing method of preparing 1,2-diols, enol acetates as well as ulosyl bromides. Overall, we believe that this one step conversion of glycals into the corresponding 1,2-diols should find wide application in organic synthesis.

Typical experimental procedure: To a solution of tribenzyl glucal (100 mg, 0.24 mmol) in 2 mL of an acetone-water (2:0.5) mixture, was added a mixture of Oxone (442 mg, 3 mmol) and $NaHCO_3$ (121 mg, 6 mmol) slowly at 20–25°C in small portions over a period of 30–60 min in a stoppered flask with continuous stirring. After the reaction was complete (TLC monitoring), acetone was evaporated and the remaining semi-solid mass was filtered and washed with EtOAc (3×15 mL). The organic layer was washed with water (2×15 mL), and brine (15 mL) and dried over Na_2SO_4. Evaporation of solvent gave the diol which was purified by column chromatography. Acetylation of the diol was done in the usual manner and the product characterised by spectroscopic and analytical means.

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References

1. Pachamuthu, K.; Paul, S.; Geyer, A.; Lokesh Babu, J.; Vankar, Y. D. *J. Org. Chem.*, submitted.
2. Fürstner, A.; Konetzki, I. *J. Org. Chem.* **1998**, *63*, 3072.
3. (a) Sanders, W. J.; Kiessling, L. L. *Tetrahedron Lett.* **1994**, *35*, 7335; (b) Shi, L.; Kim, Y.-J.; Gin, D. Y. *J. Am. Chem. Soc.* **2001**, *123*, 6939; (c) Charette, A. B.; Marcoux, J.-F.; Cote, B. *Tetrahedron Lett.* **1991**, *32*, 7215.
4. (a) Vidal, T.; Haudrechy, A.; Langlois, Y. *Tetrahedron Lett.* **1999**, *40*, 5677; (b) Hung, S.-C.; Wong, C.-H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2671; (c) Carpintero, M.; Nieto, I.; Fernandez-Mayoralas, A. *J. Org. Chem.* **2001**, *66*, 1768.
5. Barresi, F.; Hindsgual, O. *J. Am. Chem. Soc.* **1991**, *114*, 9376.
6. Stork, G.; Kim, G. *J. Am. Chem. Soc.* **1992**, *114*, 1087.
7. Bols, M. *Chem. Commun.* **1992**, 913.
8. (a) Lichtenthaler, F. W.; Schneider-Adams, T. *J. Org. Chem.* **1994**, *59*, 6728; (b) Broder, W.; Kunz, H. *Carbohydr. Res.* **1993**, *249*, 221; (c) Schmidt, R. R.; Effenberger, G. *Carbohydr. Res.* **1987**, *171*, 59; (d) Wu, E.; Wu, Q. *Carbohydr. Res.* **1993**, *250*, 327.
9. Danishefsky, S. J.; Halcomb, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 6661.
10. Iserloh, U.; Dudkin, V.; Wang, Z.-G.; Danishefsky, S. J. *Tetrahedron Lett.* **2002**, *43*, 7027.
11. Spectral and analytical data of the two new diacetates are: (corresponding to entry 3, Table 1): $[\alpha]_D = +34.6°$ (*c* 1.1, CH_2Cl_2). IR (neat) ν_{max}: 1754 cm^{-1}. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.18–7.28 (m, 10H, Ar-*H*), 6.2 (d, 1H, *J* 3.7 Hz, H-1 α-anomer), 5.52 (d, 1H, *J* 8.3 Hz, H-1 β-anomer), 4.97 (t, 1H, $J_{1,2}$ 8.3 $J_{2,3}$ 9.0 Hz, H-2 β-anomer), 4.92 (dd, 1H, $J_{1,2}$ 3.7 $J_{2,3}$ 10.0 Hz, H-2 α-anomer), 4.59–4.81 (m, 4H, CH_2Ph), 3.93 (t, 1H, $J_{2,3}$ 10.0, $J_{3,4}$ 9.7 Hz, H-3 α-anomer), 3.64 (t, 1H, $J_{2,3}$ 9, $J_{3,4}$ 9.3 Hz, H-3 β-anomer), 3.7–3.89 (m, 3H, H-6, H-6′, H-4), 3.36–3.39 (m, 1H, H-5), 2.04 and 1.91 (2s, 6H, 2× -OCOCH_3 α-anomer), 2.01 and 1.87 (2s, 6H, 2× -OCOCH_3 β-anomer), 0.8–0.84 (m, 9H, (CH_3)$_3$–SiMe$_2$–), –0.02–0.01 (m, 6H, (CH_3)$_2$Si<). ^{13}C NMR (100 MHz): δ 169.87, 169.42, 169.09, 138.32, 138.07, 138.00, 128.46, 128.44, 128.42, 128.39, 127.94, 127.87, 127.85, 127.77, 127.70, 127.59, 92.08, 89.96, 82.57, 79.84, 77.09, 76.84, 76.50, 75.45, 75.30, 75.18, 75.01, 74.11, 72.08, 71.95, 61.50, 61.44, 29.64, 25.84, 20.90, 20.83, 20.73, 20.64, 18.25, –5.13, –5.45. ESI: *m*/*z* 576 $(M+NH_4)^+$. Anal. calcd for $C_{30}H_{42}O_8Si$: C, 64.49; H, 7.58%. Found: C, 64.47; H, 7.53%.

    (Diacetate corresponding to entry 4, Table 1): $[\alpha]_D = +48°$ (*c* 1.25, CH_2Cl_2). IR (neat) ν_{max}: 1757 cm^{-1}. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.26–7.35 (m, 5H, Ar-*H*), 6.23 (d, 1H, *J* 3.9 Hz, H-1 α-anomer), 5.64 (d, 1H, *J* 8.0 Hz, H-1 β-anomer), 5.07 (dd, 1H, $J_{1,2}$ 8.0 $J_{2,3}$ 9.04 Hz, H-2 β-anomer), 5.04 (dd, 1H, $J_{1,2}$ 3.9 $J_{2,3}$ 9.5 Hz, H-2 α-anomer), 4.84 (dd, 2H, *J* 10.0, *J* 12.2 Hz CH_2Ph), 4.65 (dd, 2H, *J* 14.6, *J* 14.9 Hz CH_2Ph), 3.7–3.8 (m, 4H, H-6, H-6′, H-4, H-3 of α-anomer), 3.61 (t, 1H, $J_{2,3}$ 9.04, $J_{3,4}$ 9.28 Hz, H-3 β-anomer), 3.37–3.43 (m, 1H, H-5), 2.14 & 2.0 (2s, 6H, 2×-OC(O)CH_3 α-anomer), 2.07 and 1.97 (2s, 6H, 2×-OC(O)CH_3 β-anomer), 1.5 (d, 6H, (CH_3)$_2$C- α-anomer), 1.44 (d, 6H, (CH_3)$_2$C- β-anomer). ^{13}C NMR (100 MHz): δ 169.82, 169.35, 169.18, 138.60, 138.23, 128.28, 128.22, 127.75, 127.64, 127.51, 127.38, 99.66, 99.55, 92.44, 90.02, 78.69, 76.19, 74.38, 74.31, 73.97, 71.69, 70.99, 67.82, 65.82, 62.14, 61.85, 29.66, 29.09, 29.01, 20.91, 20.79, 20.70, 20.60, 19.07, 18.99. ESI: *m*/*z* 417 $(M+Na)^+$. Anal. calcd for $C_{20}H_{26}O_8$: C, 60.90; H, 6.64%. Found: C, 60.84; H, 6.60%.
12. Zhu, W.; Ford, W. T. *J. Org. Chem.* **1991**, *56*, 7022.