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Regioselective cleavage of the bis-benzylidene acetal of D-mannitol under oxidative and reductive conditions: a new approach to C_2-symmetric chiral ligands

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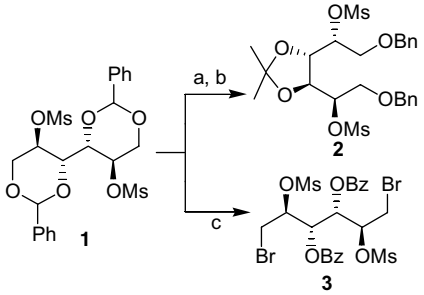
Abstract—A highly regioselective oxidative cleavage of 1,3:4,6-di-*O*-benzylidene-D-mannitol was carried out using NBS and the resultant product was readily converted to the C_2-symmetric chiral ligand, (*R*,*R*)-3,4-dihydroxy-1,5-hexadiene. On the other hand, reductive cleavage of 1,3:4,6-di-*O*-benzylidene-D-mannitol was achieved in a highly regioselective manner using $BF_3{\cdot}OEt_2$ and Et_3SiH to give a highly functionalized benzyl ether, which was converted to a synthetically useful C_2-symmetric bis-amino alcohol derivative.

Protection and deprotection of hydroxy functional groups forms an integral part of organic synthesis especially in compounds containing more than one hydroxy group.[1] The benzylidene acetal is one such functional group widely used in carbohydrate chemistry. Selective cleavage of benzylidene acetals is of importance as it leads to synthetically useful mono-protected diols. A number of reagent systems have been reported for the regioselective cleavage of benzylidene acetals.[2,3] Recently, we reported a highly regio- and chemoselective reductive cleavage of benzylidene acetals using $EtAlCl_2$–Et_3SiH.[4] The origin of the regioselectivity of the reductive ring opening can be rationalized based on steric effects and/or the chelating ability of the reagent.[5] The regioselective cleavage of a chiral bis-benzylidene acetal would be an attractive approach towards the construction of synthetically useful C_2-symmetric chiral ligands.[2i]

D-Mannitol plays an important role as a readily available chiral building block in organic synthesis.[6] In addition, mannitol and its derivatives are widely used as chiral reagents and chiral auxiliaries.[7] Our continuing interest in the stereoselective transformation of D-mannitol to biologically active and pharmaceutically important compounds,[8] recently resulted in the development of a regioselective reductive cleavage of bis-benzylidene acetal derivatives of D-mannitol to give novel chiral intermediates.[9] Herein, we report a highly regioselective cleavage of 2,5-di-mesylated-1,3:4,6-di-*O*-benzylidene D-mannitol **1**, under both reductive and oxidative conditions to give highly functionalized C_2-symmetric intermediates **2** and **3**, respectively (Scheme 1) and the further application of these novel intermediates in the



Scheme 1. Reagents and conditions: (a) $BF_3{\cdot}OEt_2$, Et_3SiH, CH_2Cl_2, 1 h. (b) 2,2-DMP, PTSA (cat), 5 h, acetone, 70% overall yield (two steps). (c) NBS, CCl_4, reflux, 30 min, 90%.

Keywords: Regioselective; Oxidative cleavage; Reductive cleavage; C_2-symmetric; Chiral ligand.
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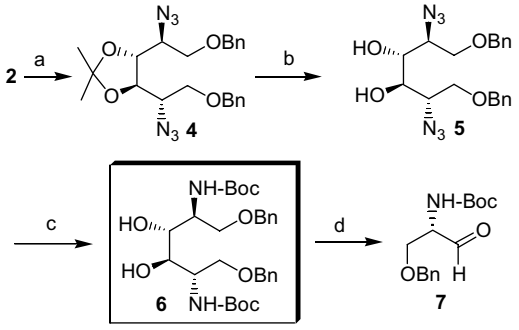
synthesis of useful chiral ligands. 2,5-Di-mesylated-1,3:4,6-di-*O*-benzylidene D-mannitol **1**[10] on regioselective cleavage, under reductive conditions with $BF_3{\cdot}OEt_2/Et_3SiH$ in dry CH_2Cl_2, gave the corresponding diol, which was protected using 2,2-dimethoxypropane in dry acetone in the presence of a catalytic amount of *p*TSA to furnish dimesylate **2** in 70% overall yield. The regioselective cleavage leading to compound **2** can be rationalized by a chelation-controlled cleavage of benzylidene acetal **1**. On the other hand, oxidative cleavage of dibenzylidene acetal **1** was achieved in a highly regioselective manner with NBS in dry CCl_4,[3a,b] in the presence of an incandescent lamp, to give dibromo derivative **3**. As expected attack of bromide ion on the less hindered sites resulted in the formation of compound **3**.

Compounds **2** and **3** are highly functionalized C_2-symmetric chiral intermediates and have scope for further functional group manipulation to provide novel chiral intermediates. Capitalizing on our highly regioselective cleavage methodology, we have developed an efficient method for the stereoselective synthesis of the C_2-symmetric chiral bis-amino alcohol derivative **6** as shown in Scheme 2.

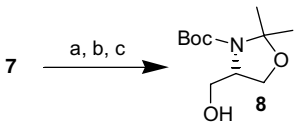


Scheme 2. Reagents and conditions: (a) NaN_3, DMF, 110 °C, 24 h, 91%. (b) CSA (cat.), MeOH, reflux, 24 h, 85%. (c) Lindlar's catalyst, H_2 (1 atm), Boc_2O, MeOH, rt, 2 h, 93%. (d) $NaIO_4/SiO_2$, CH_2Cl_2, rt, 2 h, 93%.

Thus, nucleophilic displacement of the dimesylate **2** by sodium azide afforded the corresponding diazide **4**, which upon treatment with CSA in methanol gave the azido-alcohol **5**. Chemoselective reduction of azido-alcohol **5** using Lindlar's catalyst in the presence of Boc_2O afforded the corresponding *N*,*N*′-di-Boc derivative **6**[11] an analogue of HIV protease as well as glycosidase inhibitors.[12]

Oxidative cleavage of compound **6** using $NaIO_4$ supported on silica gel[13] afforded the chiral building block (*S*)-2-(*N*-butoxycarbonyl)-3-*O*-benzylserinal **7**[14] $\{[\alpha]_D^{25}$ +36.3 (*c* 1.0, CH_2Cl_2)} in excellent yield.

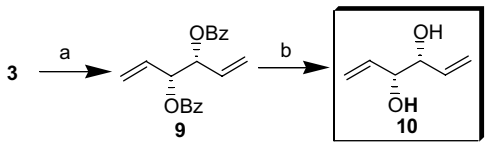
The observed optical rotation of the serinal derivative **7** is not in agreement with the reported value.[15] Since α-amino aldehydes are very labile and prone to undergo racemization,[14b] the chiral integrity of our (*S*)-2-(*N*-butoxycarbonyl)-3-*O*-benzyl serinal **7** was established by converting it to the known compound **8** in three steps (Scheme 3). The optical rotation of the alcohol **8** was found to be in accordance with the reported value $\{[\alpha]_D^{25}$ +23.3 (*c* 1.4, $CHCl_3$)}.[16] This indirectly vindicates the optical purity of the serine aldehyde derivative **7**. This is a practical approach for the racemization-free synthesis of the serinal derivative **7** starting from the readily available D-mannitol.



Scheme 3. Reagents and conditions: (a) $NaBH_4$, MeOH, −20 °C, 92%. (b) 2,2-DMP, $BF_3{\cdot}OEt_2$, 0 °C, 88%. (c) Pd/C–H_2, MeOH, 95%.

On the other hand, compound **3** was readily converted to the C_2-symmetric (*R*,*R*)-3,4-dihydroxy-1,5-hexadiene **10**, an important intermediate in natural product synthesis. Chiral 1,2-divinyl glycols have drawn considerable attention in recent years as useful building blocks[17]owing to their inherent C_2-symmetry.

Thus, reductive elimination of the key intermediate 1,6-di-deoxydibromo derivative **3** with zinc, followed by hydrolysis of **9** with K_2CO_3 in methanol, furnished (*R*,*R*)-3,4-dihydroxy-1,5-hexadiene **10** in excellent yield (Scheme 4). The spectral data of **10** $\{[\alpha]_D^{25}$ +32·6 (*c* 1.0, $CHCl_3$)} are in accordance with reported data.[18]



Scheme 4. Reagents and conditions: (a) Zn dust, EtOH, reflux, 6 h, 84%. (b) K_2CO_3, MeOH, rt, 1 h, 98%.

In summary, we have developed a highly regioselective cleavage of 2,5-di-mesylated-1,3:4,6-di-*O*-benzylidene D-mannitol **1** under both oxidative and reductive conditions. The potential application of the novel key intermediates **2** and **3**, was exemplified in the stereoselective synthesis of C_2-symmetric chiral bis-amino alcohol derivative **6** and (*R*,*R*)-3,4-dihydroxy-1,5-hexadiene **10**, respectively.[19]

*Experimental procedure for reductive cleavage of 2,5-di-mesylated-1,3:4,6-di-O-benzylidene-*D*-mannitol **1** with Et_3SiH and $BF_3{\cdot}OEt_2$.* To a solution of 1,3:4,6-di-*O*-benzylidene-D-mannitol **1** (4.1 g, 8 mmol) in dry CH_2Cl_2 (100 mL) at 0 °C was added Et_3SiH (2.8 mL, 17.5 mmol) followed by $BF_3{\cdot}Et_2O$ (3.2 mL, 25.5 mmol). After stirring the reaction mixture at 0 °C for 1 h, it was quenched with saturated $NaHCO_3$ solution (20 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude compound was azeotropically dried with toluene, re-dissolved in dry acetone (20 mL) and then treated with 2,2-dimethoxypropane (2.9 mL, 23.7 mmol) followed by a solution

of *p*TSA in dry acetone (5 mL). The resultant mixture was allowed to stir for 5 h at room temperature. The mixture was then diluted with EtOAc (20 mL), washed with a saturated solution of $NaHCO_3$ (2 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield a crude compound, which was purified by column chromatography on silica gel (gradient elution with 15–25% EtOAc in hexane) to give pure dimesylate **2**[9] (3.1 g, 70% overall yield). $[\alpha]_D^{25}$ +28.6 (*c* 1.0, $CHCl_3$); IR (neat): 1356, 1177 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 6H), 2.98 (s, 6H), 3.65 (dd, J = 7.3, 11.2 Hz, 2H), 3.79 (dd, J = 3.4, 11.7 Hz, 2H), 4.27 (d, J = 4.8 Hz, 2H), 4.47 (AB quartet, J = 11.7 Hz, 4H), 4.78–4.82 (m, 2H), 7.18–7.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 38.5, 68.6, 73.2, 76.4, 80.2, 111.0, 127.6, 127.7, 128.3, 137.1; MS (EI) *m/z* (relative intensity, %) 558 (32) (M+), 557 (10), 467 (23), 379 (15), 181 (100), 111 (20), 91 (60). HRMS (ESI) calcd for $C_{25}H_{34}O_{10}S_2Na$ $(M+Na)^+$: 581.1491; found: 581.1489.

*Experimental procedure for oxidative cleavage of 2,5-dimesylated-1,3:4,6-di-O-benzylidene-*D*-mannitol **1** with NBS*. To a solution of dibenzylidene acetal **1** (1.03 g, 2 mmol) in dry CCl_4 (60 mL) was added *N*-bromosuccinimide (854 mg, 4.8 mmol) and the resultant mixture was refluxed under a nitrogen atmosphere in the presence of incandescent light for 30 min. After completion of the reaction, as indicated by TLC (ca. 1 h), the reaction mixture was cooled to room temperature and diluted with 20 mL CH_2Cl_2. The organic layer was then washed with saturated aqueous $NaHCO_3$ solution (2 × 30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the crude compound, which was purified by column chromatography on silica gel (gradient elution with 20–30% EtOAc in hexane) to furnish pure bromomesylate **3** as a white foamy solid (1.2 g, 90% yield). $[\alpha]_D^{25} = +46.4$ (*c* 1.0, $CHCl_3$); IR (KBr): 1729, 1361, 1255 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.04 (s, 6H), 3.66 (dd, J = 12.2, 11.7 Hz, 2H), 3.88 (dd, J = 12.2, 11.7 Hz, 2H), 5.24 (m, 2H), 5.81 (d, J = 5.9 Hz, 2H), 7.39–7.58 (m, 4H), 8.00–8.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 39.0, 69.0, 128.9, 130.2, 134.2, 165.3; HRMS (FAB) calcd for $C_{22}H_{24}O_{10}S_2Br_2Na$ $(M+Na)^+$ 692.9075; found 692.9057.

Acknowledgements

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Compound **4**: $[\alpha]_D^{25}$ +65.4 (*c* 1.0, $CHCl_3$); IR (neat): 2112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 6H), 3.43–3.46 (m, 2H), 3.67 (dd, J = 10.2, 4.8 Hz, 2H), 3.74 (dd, J = 10.2, 7.8 Hz, 2H), 4.23 (br s, 2H), 4.67 (AB quartet, J = 11.7 Hz, 4H), 7.26–7.36 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 60.2, 70.0, 73.6, 76.8, 110.5, 127.8, 128.0, 128.6, 137.5; HRMS (FAB) calcd for $C_{23}H_{28}N_6O_4Na$ $(M+Na)^+$ 475.2070; found 475.2053.
Compound **5**: $[\alpha]_D^{25}$ +43.3 (*c* 1.0, $CHCl_3$); IR (neat): 3472, 2112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.06 (br s, 2H), 3.62–3.70 (m, 2H), 3.77–3.82 (m, 6H), 4.56–4.62 (m, 4H), 7.28–7.37 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.6, 70.0, 71.2, 73.7, 127.8, 128.0, 128.6, 137.3; MS (FAB) *m/z* (relative intensity, %) 435 (10) $(M+Na)^+$, 385 (70), 351 (15), 302 (12), 181 (25), 165 (35), 150 (90), 133 (100).
Compound **6**: $[\alpha]_D^{25}$ +7.2 (*c* 1.0, $CHCl_3$); IR (neat): 3328, 1673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 18H), 3.09 (br s, 2H), 3.62 (br s, 4H), 3.76 (s, 2H), 4.07 (br s, 2H), 4.51 (AB quartet, J = 11.7 Hz, 4H), 5.16 (br s, 2H), 7.34–7.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2, 50.3, 71.2, 71.9, 73.1, 79.5, 127.7, 128.4, 137.7, 156.0; MS (FAB) *m/z* (relative intensity, %) 583 (15) $(M+Na)^+$, 461 (10), 405 (85), 361 (50), 327 (20), 281 (20), 222 (25), 207 (40), 193 (25), 147 (100), 133 (75), 123 (85).
Compound **7**: $[\alpha]_D^{25}$ +36.3 (*c* 1.0, CH_2Cl_2); IR (neat): 3408, 1705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 9H), 3.70 (dd, J = 4.0, 9.6 Hz, 1H), 3.99 (dd, J = 2.4, 9.4 Hz, 1H), 4.32 (m, 1H), 4.50 (AB quartet, J = 12.0 Hz, 2H), 7.26–7.36 (m, 5H), 9.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 60.0, 67.8, 73.5, 80.2, 127.6, 127.9, 128.5, 137.2, 155.6, 199.1.
Compound **9**: $[\alpha]_D^{25}$ +99.7 (*c* 1.0, acetone); IR (neat): 1721, 1630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)δ 5.34 (d, J = 10.7 Hz, 2H), 5.46 (d, J = 17.6 Hz, 2H), 5.80 (m, 2H), 5.92–5.99 (m, 2H), 7.34–8.04 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.0, 119.6, 128.4, 129.7, 129.9, 132.0, 133.1, 165.4; MS (EI) *m/z* (relative intensity, %) 322 (M^+, 20), 281 (6.8), 161 (9.5), 144 (54.8), 105 (100), 77 (48), 51 (9.5).
Compound **10**. $[\alpha]_D^{25}$ +32.6 (*c* 1.0, $CHCl_3$); IR (neat): 3376, 1638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 2H), 3.93–3.96 (m, 2H), 5.18 (d, J = 10.5 Hz, 2H), 5.28 (d, J = 17.2 Hz, 2H), 5.76–5.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.7, 117.2, 136.5.