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# Stereoselective ring-opening reactions with AcBr and AcCl. A new method for preparation of some haloconduritols

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**Abstract**—The actions of AcX (X=Br, Cl) on 7-oxa-bicyclo[2.2.1]hept-5-ene-2,3-diol diacetates and a *transoid*-epoxide prepared from the acetonide of cyclohexa-3,5-diene-*cis*-1,2-diol were studied. $H_2SO_4$-catalyzed cleavage of *exo-cis*-7-oxa-bicyclo[2.2.1]hept-5-ene-2,3-diol diacetate with AcCl gave (1α,2α,3α,6β)-6-chloro-4-cyclohexene-1,2,3-triol triacetate, from which the corresponding chloroconduritol was obtained by *trans*-esterification (MeOH/HCl). A similar reaction of the *exo*-diacetate with AcBr in the presence of $H_2SO_4$ resulted in bromine addition. The formation of bromine from the reaction of AcBr and $H_2SO_4$ was observed by independent experiments. $H_2SO_4$-catalyzed reaction of *endo-cis*-7-oxa-bicyclo[2.2.1]hept-5-ene-2,3-diol diacetate with AcX (X=Br, Cl) gave (1α,2α,3β,6β)-6-halo-4-cyclohexene-1,2,3-triol triacetates. The reaction of the *transoid*-epoxide with AcX (X=Br, Cl) with no catalyst gave also (1α,2α,3β,6β)-6-halo-4-cyclohexene-1,2,3-triol triacetates.


## 1. Introduction

Glycosidase inhibitors have become interesting as anti-obesity drugs, antidiabetics, antifungals, insecticides, and antivirals, including substances active against the human immunodeficiency virus (HIV) and metastasis.[1] Bromo-conduritol, a diastereomeric mixture of (1α,2β,3α,6β)-6-bromo-4-cyclohexene-1,2,3-triol and (1α,2β,3α,6α)-6-bromo-4-cyclohexene-1,2,3-triol, has been commonly used as a covalent, irreversible, active-site directed glucosidase inhibitor.[2]

A few synthetic procedures[2d,3] for the preparation of haloconduritols have been described. Recently, we have reported[4] a facile synthesis of haloconduritols based on Lewis acid ($BBr_3$ or $BCl_3$)-assisted ring-opening of *endo*-diacetate **1** at low temperature. Thus, our method gives haloconduritol diacetates **2a**, **3a** in the construction of conduritol-A, from which haloconduritols **2c**, **3c** were efficiently prepared (Scheme 1).

Mechanistic investigations have revealed that ring-opening of *endo*-diacetate **1** proceeds by a neighboring group participation. A neighboring group participation is not expected in *exo*-diacetate **4** due to the relative stereochemistry. Ring-opening of *exo*-diacetate **4** should afford a different haloconduritol. Thus, we planned to investigate the ring-opening of *exo*-diacetate **4**. Also, considering high reactivity of epoxides to give halohydrins, we studied the ring-opening reactions of epoxide **5** to give haloconduritols (Fig. 1).

## 2. Results and discussion

At first, we attempted the $BX_3$-assisted ring-opening of *exo*-diacetate **4**. We treated *exo*-diacetate **4** with $BBr_3$ or $BCl_3$ at −78 °C and then, the reaction mixture was stirred at room temperature for 4 h. After quenching the reaction with water and chromatographic separation, we determined that the reaction with $BBr_3$ gave three products (**6**, **7**, and **8**) Attempts to ring-open **4** with $BCl_3$ were unsuccessful (Scheme 2).

The formation of **6**–**8** may be explained via haloboranation. Haloboranation of olefins with $BBr_3$ has been known[5] for a long time. Formation of monobromide **6** and **7** may be easily explained by addition of $BBr_3$ to the double bond of **4** to give Br–C–C–$BBr_2$-like intermediates **9** and **10** followed by hydrolysis. The formation of **8** probably proceeds through the oxidation of C–B bond of intermediate **10** by air oxygen to give **11** (Scheme 3). Indeed, performing the reaction under $N_2$ atmosphere and quenching the reaction media with water gave only dibromides **6** and **7** in a ratio of 1:1 and total yield of 65%.

Cleavage of ethers by acyl halides have been known for over

*Keywords*: Haloconduritol; Ring-opening; 7-Oxa-bicyclo[2.2.1]hept-5-ene-2,3-diol diacetate; Cyclohexa-3,5-diene-*cis*-1,2-diol; Acetyl bromide; Acetyl chloride.
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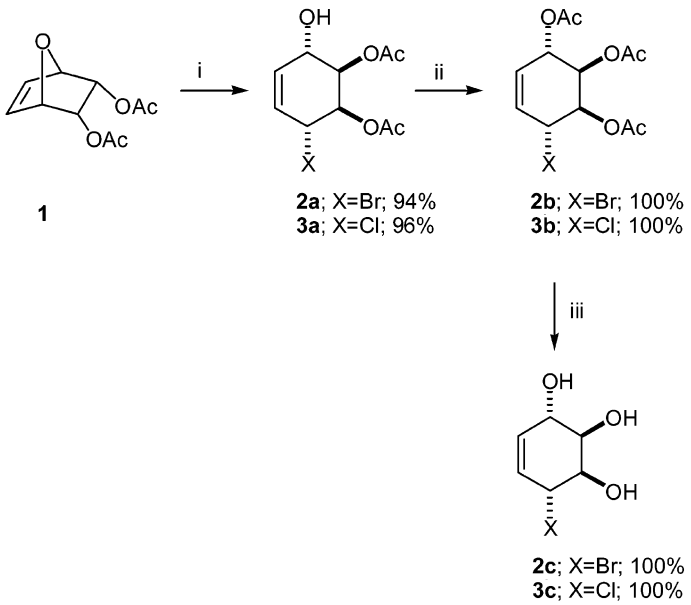



**Scheme 1.** (i) $BX_3$, $CH_2Cl_2$, −78 °C, then $H_2O$ ($BX_3$=$BBr_3$ or $BCl_3$) (ii) $CH_3COCl$, $CH_2Cl_2$; (iii) MeOH, HCl, 0 °C.

50 years.[6] Considering the efficiency of the reaction to give alkyl halides and alcohols we applied this method to *exo*-diacetate **4**. For this, we treated *exo*-diacetate **4** with excess AcCl in the presence of $H_2SO_4$. As expected, the reaction gave chloroconduritol triacetate **13a** in the construction of conduritol-C, from which chloroconduritol **13b** was readily obtained by *trans*-esterification. The $^1H$ NMR spectra of **13a**,**b** showed an identity with similar C-type haloconduritol derivatives.[3c,7] As a surprising result, the reaction of *exo*-diacetate **4** with AcBr and $H_2SO_4$ gave a brominated compound **12** (Scheme 4).

We assumed that brominated compound **12** should be formed via addition of $Br_2$ to the double bond of **4**. As evidence, one drop of $Br_2$ was added to a solution of *exo*-diacetate **4** in $CDCl_3$ in an NMR tube, and the NMR spectra showed the formation **12** as a sole product. To our knowledge, there has not been any report on the formation of bromine from the reaction of AcBr and $H_2SO_4$. Therefore, the formation of bromine from AcBr and $H_2SO_4$ was provided by performing an independent experiment. To a stirred solution of 50 mmol AcBr in $CH_2Cl_2$ was added one drop $H_2SO_4$ and the reaction mixture was additionally stirred for 15 min. Meanwhile the colorless reaction mixture turned red. To determine the quantity of the bromine, 25 mmol cyclohexene was added and after purification only 0.8 mmol 1,2-dibromocyclohexane was obtained. In another experiment, after treatment of 50 mmol AcBr with 50 mmol $H_2SO_4$ in dichloromethane, 25 mmol cyclohexene was added to reaction mixture. This time, isolated 1,2-dibromocyclohexane was 22 mmol. These findings show that the decomposition of AcBr with $H_2SO_4$ is not a catalytic reaction. Most probably, $H_2SO_4$ seems to participate in the reaction as a reagent. At this stage we did not study the mechanism of the reaction.

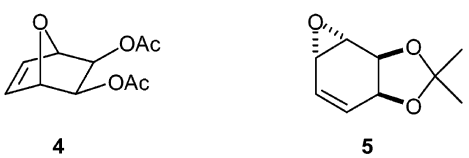
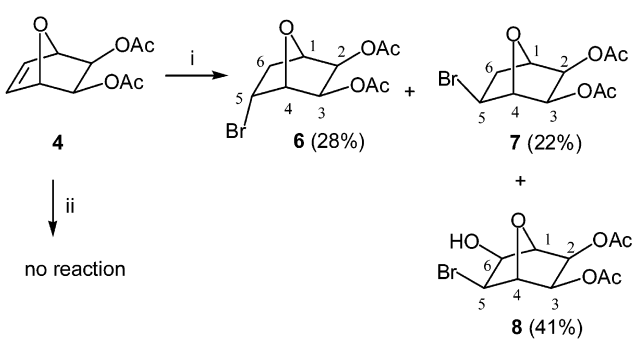


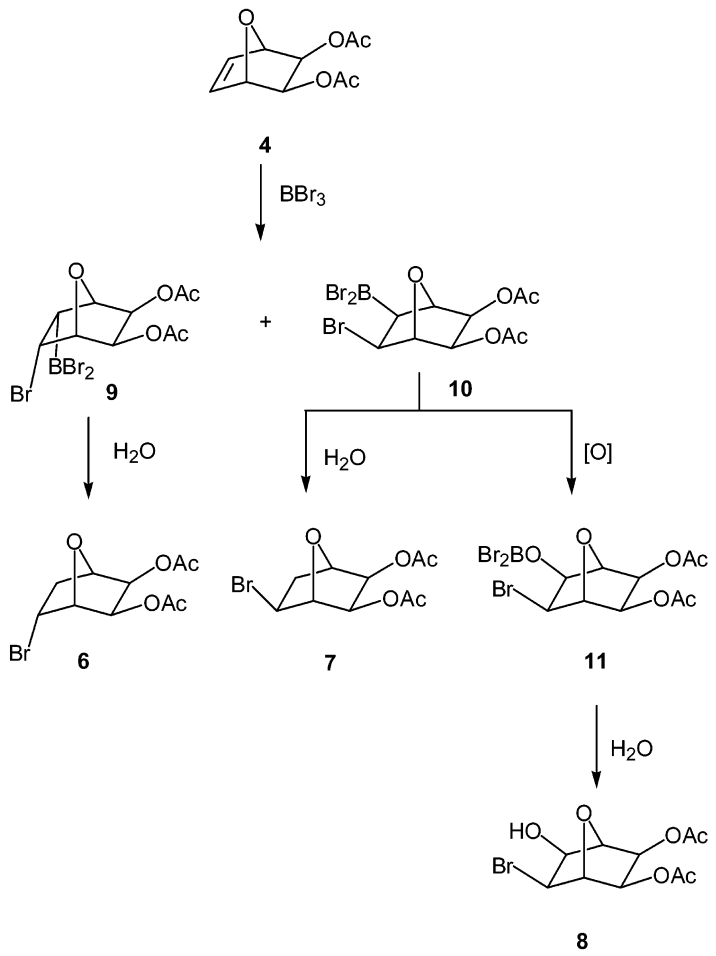

**Figure 1.**

Complete peak assignments of the NMR spectra of **6**, **7**, **8** and **12** were carried out. Taking into consideration the coupling constants, we easily elucidated the relative stereochemistry of $H_2$, $H_3$, $H_5$ and $H_6$. In the $^1H$ NMR spectra of these four compounds $J_{1,2}$ and $J_{3,4}$ were not observed probably due to dihedral angles close to 90°. Similar results were reported in benzobicylic[2.2.1]system having *exo*-substituents.[8] Again, all $J_{2,3}$ values are about 6.2 Hz. $J_{5,6}$ of **8**, similar to $J_{2,3}$, is also 6.3 Hz. While *endo*-$H_5$ of **7** is seen as a doublet of doublets ($J_{5,6endo}$=7.0 Hz, $J_{5,6exo}$=4.0 Hz), *exo*-$H_5$ of **6** is seen as doublet of triplets ($J_{5,6exo}$=10.9 Hz, $J_{5,6endo}$=5.0 Hz, $J_{4,5}$=5.0 Hz). The configurations of the groups in **7** and **8** were also confirmed by the observation of NOE effects. In **7**, irradiation of H–$C_5$(Br) at $\delta$ 4.03 caused signal enhancement of the resonances at $H_2$, $H_3$ and adjacent protons at $C_6$. In a similar way, irradiation of H–$C_6$(OH) of **8** at $\delta$ 3.94 caused signal enhancement of the resonances at $H_1$, $H_2$, $H_3$ and $H_5$.

In our previous studies, $BBr_3$ or $BCl_3$-assisted ring-opening of *endo*-diacetate **1** required a temperature of −78 °C.




**Scheme 2.** (i) $BBr_3$, $CH_2Cl_2$, −78 °C, then $H_2O$ (ii) $BCl_3$, $CH_2Cl_2$, −78 °C, then $H_2O$.

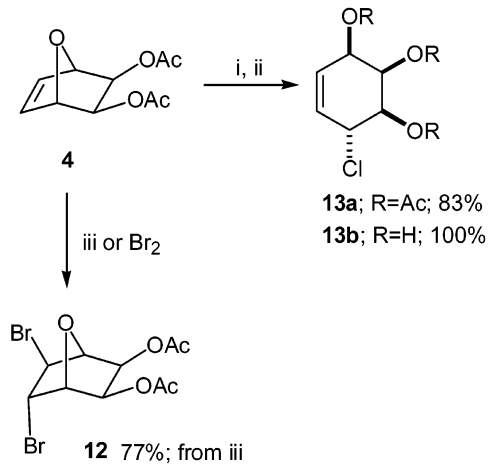



**Scheme 3.** Possible mechanism for the formation **6**–**8** from **4**.

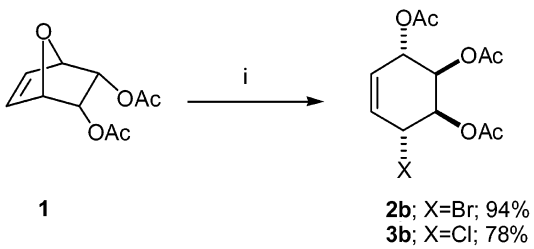
Therefore we attempted to ring-opening of **1** with AcX (X=Br, Cl) at ambient temperature. The reaction gave haloconduritol triacetates **2b** and **3b** in good yields (Scheme 5). The reaction appears to proceed by neighboring group participation as with the reaction in Scheme 1.

Epoxide **5**, readily prepared by epoxidation of acetonide **14**, is highly reactive to substitution and has been used for many syntheses in the literature.[9] Without any catalyst, the reaction of epoxide **5** with excess of acetyl halides (X=Br, Cl) gave directly **2b** and **3b** in good yields (Scheme 6).

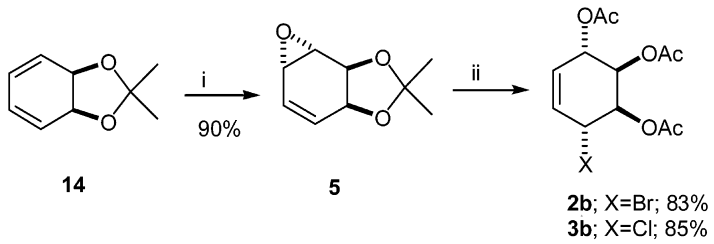
We suppose that the formation of products **2b** and **3b** proceeds by an $S_N2'$ mechanism as outlined in Scheme 7. At first, epoxide **5** and acetyl halide should give a **15**-like tetrahedral intermediate. While halide is being transferred to the 6-position, the electron pair of the double bond could substitute carbon–oxygen bond of epoxide at $C_4$ to give **16**-like product. Further acetylation of ketal oxygens with acetyl halide affords haloconduritol triacetates **2b** and **3b**. Similar $S_N2'$ substitutions were observed in the reactions of **5** or **5**-like unsaturated epoxides with some organometallic reagents.[10]




**Scheme 4.** (i) AcCl, $CH_2Cl_2$, $H_2SO_4$; (ii) MeOH, HCl; (iii) AcBr, $CH_2Cl_2$, $H_2SO_4$.




**Scheme 5.** (i) AcX (X=Br, Cl), $CH_2Cl_2$, $H_2SO_4$ (cat).




**Scheme 6.** (i) MCPBA, (ii) AcX (X=Br, Cl), $CH_2Cl_2$.

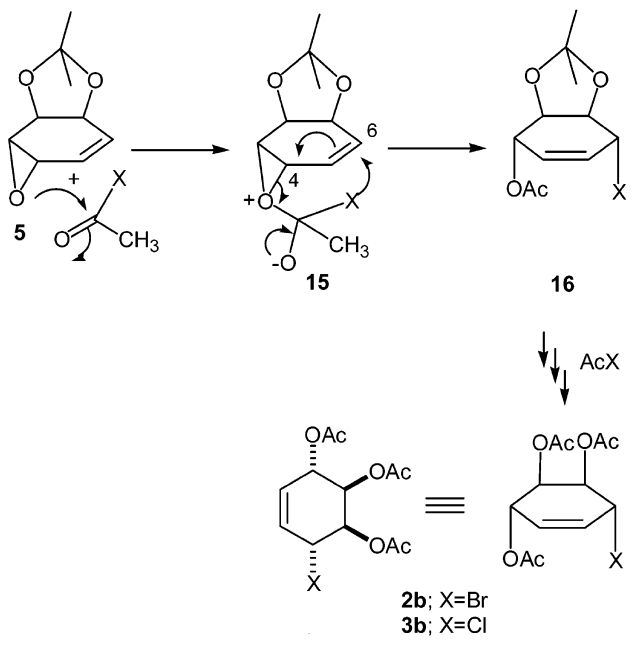
## 3. Conclusion

In conclusion, we describe in this paper a preparation method for a new chloroconduritol **13b** in the construction of conduritol-C. We also describe two new methods for the preparation of haloconduritol triacetates **2b** and **3b** from *endo*-diacetate **1** and epoxide **5** via cleavage with acetyl halides. Deacetylation of triacetates **2b** and **3b** by *trans*-esterification (MeOH/HCl) to give the corresponding haloconduritols was reported in our previous paper.[4]

## 4. Experimental

### 4.1. General information

Solvents were purified and dried by standard procedures before use. Melting points were determined on Büchi 539 capillary melting apparatus and uncorrected. Infrared spectra were obtained from KBr pellets or film on a Mattson 1000 FT-IR spectrophotometer. The $^1H$ and $^{13}C$ NMR spectra were recorded on 200 (50) MHz Varian spectrometers. Elemental analyses were carried out on a Carlo Erba 1108 model CHNS-O analyser. Column chromatography was performed on silica gel 60 (70–230 mesh ASTM). Thin layer chromatography was carried out on Merck 0.2 mm silica gel, 60 $F_{254}$ analytical aluminum plates.




**Scheme 7.** Suggested mechanism for the formation of **2b** and **3b** from epoxide **5**.

**4.1.1. *endo-cis*-7-Oxa-bicyclo[2.2.1]heptane-2,3-diol diacetate (1).**[4] **1** was prepared from *endo*-cycloadduct of furan and vinylene carbonate according to our previously reported procedure.[4]

**4.1.2. *exo-cis*-7-Oxa-bicyclo[2.2.1]heptane-2,3-diol diacetate (4).**[4] **4** was prepared from *exo*-cycloadduct of furan and vinylene carbonate according to our previously reported procedure.[4]

**4.1.3. *cis*-1,2-Isopropylidenedioxycyclohexa-3,5-diene (14).** Acetonide **14** was prepared from 1,4-cyclohexadiene as described by Yang[11] et al. A direct preparation of **14** from cyclohexa-3,5-diene-*cis*-1,2-diol in a high yield is also described by Ramesh[9b] et al.

**4.1.4. (3aα,5aβ,6aβ,6bα)-2,2-dimethyl-3a,5a,6a,6b-tetrahydro-oxireno[*e*]-1,3-benzo-dioxole (5).** Epoxide **5** was prepared by epoxidation of acetonide **14** with *m*-chloroperbenzoic acid following the reported procedure by Banwell[9f] et al.

**4.1.5. The reaction of *exo*-diacetate 4 with $BBr_3$.** *Method A*. Under nitrogen atmosphere, to a stirred solution of *exo*-diacetate **4** (1.00 g, 4.7 mmol) in 20 mL of $CH_2Cl_2$ was added dropwise a solution of $BBr_3$ (0.5 mL, 1.30 g, 5.2 mmol) in 20 mL of $CH_2Cl_2$ at −78 °C over 10 min. After addition was completed, the mixture was stirred at 0 °C for 1 h, and then at room temperature for 4 h under air atmosphere. To the reaction mixture was added 5 mL of saturated $NaHCO_3$ solution. The organic phase was separated. The aqueous phase was additionally extracted with $CHCl_3$ (3×30 mL). The combined organic phases were dried over $Na_2SO_4$. The solvent was evaporated (30 °C, 25 mm Hg) and the product was chromatographied on a silica gel column (70 g) eluting with hexane–EtOAc (3:1).

*The first fraction* (2*exo*,3*exo*,5*endo*)-5-*Bromo*-7-*oxa*-*bicyclo*[2.2.1]*heptan*-2,3-*diol diacetate* (**6**). (0.40 g, %28). Colorless crystal. Mp 125–127 °C (solidified). $^1H$ NMR (200 MHz, $CDCl_3$) δ 5.66 (d, 1H, $H_3$, $J_{2,3}$=6.2 Hz), 4.97 (d, 1H, $H_2$, $J_{2,3}$=6.2 Hz), 4.50 (d, 1H, $H_4$, $J_{4,5}$=5.0 Hz), 4.42 (d, 1H, $H_1$, $J_{1,6exo}$=6.2 Hz), 3.98 (dt, 1H, $H_5$, $J_{5,6exo}$=10.9 Hz, $J_{5,6endo}$=5.0 Hz, $J_{4,5}$=5.0 Hz), 2.53 (ddd, 1H, $H_6$ (*exo*), $J_{6endo,6exo}$=15.9 Hz, $J_{5,6exo}$=10.9 Hz, $J_{1,6exo}$=6.2 Hz), 1.65 (dd, 1H, $H_6$ (*endo*), $J_{6endo,6exo}$=15.9 Hz, $J_{5,6endo}$=5.0 Hz), 2.12 (s, 3H), 2.08 (s, 3H). $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 171.3 (2C), 83.9, 82.7, 77.4, 75.8, 41.6, 38.4, 22.4, 22.3. IR (KBr) 2993, 2923, 2854, 1747, 1438, 1388, 1245, 1130, 1064, 1041, 906 $cm^{-1}$. Anal. calcd for $C_{10}H_{13}BrO_5$ (293.11): C, 40.98; H, 4.47; Found: C, 40.61, H, 4.35.

*Second fraction* (2*exo*,3*exo*,5*exo*)-5-*Bromo*-7-*oxa-bicyclo* [2.2.1]*heptan*-2,3-*diol diacetate* (**7**). (0.30 g, %22). Colorless crystal. Mp 134–136 °C (solidified). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.87 (A part of AB system, d, 1H, $H_2$ or $H_3$, $J_{2,3}$=6.2 Hz), 4.80 (B part of AB system, d, 1H, $H_2$ or $H_3$, $J_{2,3}$=6.2 Hz), 4.60 (br d, 1H, $H_1$, $J_{1,6exo}$=5.0 Hz), 4.56 (br s, 1H, $H_4$), 4.03 (dd, 1H, $H_5$, $J_{5,6endo}$=7.0 Hz, $J_{5,6exo}$=4.0 Hz), 2.27–2.06 (AB system, m, 2H, $H_6$ (*endo*) and $H_6$ (*exo*)), 2.06 (s, 6H). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 172.1, 171.8, 88.8, 81.8, 76.9, 75.3, 44.4, 40.5, 22.5, 22.4. IR (KBr) 3031, 3012, 1747, 1438, 1388, 1373, 1257, 1218, 1195, 1141, 1064, 1002, 944, 898 cm$^{-1}$. Anal. calcd for $C_{10}H_{13}BrO_5$ (293.11): C, 40.98; H, 4.47; Found: C, 40.51, H, 4.64.

*Third fraction* (2*exo*,3*exo*,5*exo*,6*exo*)-5-*Bromo*-7-*oxa-bicyclo*[2.2.1] *heptan*-2,3,6-*triol* 2,3-*diacetate* (**8**). (0.60 g, %41). Colorless crystal. Mp 149–151 °C (solidified). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 4.94 (A part of AB system, d, 1H, $H_2$ or $H_3$, $J_{2,3}$=6.2 Hz), 4.91 (B part of AB system, d, 1H, $H_2$ or $H_3$, $J_{2,3}$=6.2 Hz), 4.56 (br d, 1H, $H_4$, $J_{1,4}$=2.2 Hz), 4.41 (d, 1H, $H_1$, $J_{1,4}$=2.2 Hz), 4.27 (d, 1H, $H_5$, $J_{5,6}$=6.3 Hz), 3.94 (dd, 1H, $H_6$, $J_{5,6}$=6.3 Hz, $J_{6,OH}$=9.5 Hz), 2.35 (d, 1H, OH, $J_{6,OH}$=9.5 Hz), 2.10 (s, 3H), 2.09 (s, 3H). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 171.5, 171.4, 89.0, 88.4, 74.8, 73.5, 72.1, 55.0, 22.3 (2C). IR (KBr) 3455, 3394, 1643, 1554, 1469, 1427, 1052, 1025, 964 cm$^{-1}$. Anal. calcd for $C_{10}H_{13}BrO_6$ (309.11): C, 38.86; H, 4.24; Found: C, 39.10, H, 4.31.

*Method B*. Under nitrogen atmosphere, to a stirred solution of *exo*-diacetate **4** (0.160 g, 0.75 mmol) in 20 mL of $CH_2Cl_2$ was added dropwise a solution of $BBr_3$ (0.1 mL, 0.26 g, 1.0 mmol) in 20 mL of $CH_2Cl_2$ at −78 °C over 10 min. After addition was completed, the mixture was stirred at 0 °C for 1 h, and then at room temperature for 4 h under nitrogen atmosphere. After quenching of the reaction mixture with water (1 mL), organic phase was separated, dried ($Na_2SO_4$). Removing of the solvents gave a mixture of monobromides **6** and **7** in a ratio of 1: 1 (according to $^1$H NMR) (0.143 g; 65%).

**4.1.6. (1α,2α,3α,6β)-6-Chloro-4-cyclohexene-1,2,3-triol triacetate (13a).** To a solution of *exo*-diacetate **4** (0.50 g, 2.36 mmol) in $CH_2Cl_2$ (5 mL) were added 1.5 mL of AcCl and one drop $H_2SO_4$. The reaction mixture was stirred for 24 h at room temperature. The solvent and excess of AcCl were evaporated. The residue was dissolved in $CHCl_3$ and the solution filtered over an basic $Al_2O_3$ (Aktiv.1; 5 g). Removal of the solvent gave **13a** (0.57 g, 83%). Colorless crystal. Mp 103–104 °C (from hexane–EtOAc). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.90 (dt, 1H, $H_5$, $J$=10.5, 2.6 Hz), 5.69–5.58 (m, 3H, $H_2$, $H_3$ and $H_4$). 5.22 (dd, 1H, $H_1$, $J_{1,6}$=8.4 Hz, $J_{1,2}$=2.0 Hz), 4.72 (dm, 1H, $H_6$, $J_{1,6}$=8.4 Hz), 2.11 (s, 3H), 2.10 (s, 3H), 2.03 (s, 3H). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 171.9, 171.5 (2C), 131.5, 128.4, 75.4, 71.1, 69.4, 56.7, 22.6 (3C). IR (KBr) 2969, 1754, 1430, 1373, 1226, 1157, 1075, 1033, 917 cm$^{-1}$. Anal. calcd for $C_{12}H_{15}ClO_6$ (290.70): C, 49.58; H, 5.20; Found: C, 49.38, H, 5.16.

**4.1.7. (1α,2α,3α,6β)-6-Chloro-4-cyclohexene-1,2,3-triol (13b).** A stirred solution of **13a** (0.35 g, 1.20 mmol) in 20 mL of methanol was cooled to 0 °C. At the given temperature HCl gas was passed through the solution over 20 min. The reaction flask was closed with a stopper and stirred at room temperature for 1 h. Removal of the solvent, methyl acetate and HCl under reduced pressure (30 °C, 25 mm Hg) and recrystallization from EtOAc gave chloroconduritol **13b** (0.16 g, 82%). Colorless crystal. Mp 128–130 °C (from EtOAc). $^1$H NMR (200 MHz, DMSO-$d_6$) $\delta$ 5.63–5.49 (AB system, 2H, $H_4$ and $H_5$, $J_{4,5}$=10.5 Hz), 4.54 (br d, 1H, $H_6$, $J_{1,6}$=7.4 Hz), 4.16–3.96 (m, 4H, 3×OH and $H_2$), 3.82 (br s, 1H, $H_3$), 3.59 (br d, 1H, $H_1$, $J$=7.4 Hz). $^{13}$C NMR (200 MHz, DMSO-$d_6$) $\delta$ 133.5, 128.5, 76.4, 74.4, 69.3, 63.6. IR (film) 3326, 2929, 2894, 1428, 1351, 1312, 1258, 1150, 1027, 927, 888, 850 cm$^{-1}$. Anal. calcd for $C_6H_9ClO_3$ (164.59): C, 43.78; H, 5.51; Found: C, 43.58, H, 5.53.

**4.1.8. (2*exo*,3*exo*,5*endo*,6*exo*)-5,6-Dibromo-7-oxa-bicyclo [2.2.1] heptan-2,3-diol diacetate (12).** To a solution of *exo*-diacetate **4** (0.25 g, 1.18 mmol) in $CH_2Cl_2$ (5 mL) were added 1 mL of AcBr and one drop $H_2SO_4$. The reaction mixture was stirred for 12 h at room temperature. The solvent and excess of AcBr were evaporated. The residue was dissolved in $CHCl_3$ and the solution filtered over an basic $Al_2O_3$ (Aktiv.1; 5 g). Removal of the solvent gave dibromide **12** (0.34 g, 77%). Colorless crystal. Mp 99–101 °C (from hexane–EtOAc). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.65 (d, 1H, $H_3$, $J_{2,3}$=6.2 Hz), 5.06 (d, 1H, $H_2$, $J_{2,3}$=6.2 Hz), 4.64 (br d, 1H, $H_4$, $J_{4,5}$=5.4 Hz), 4.54 (br s, 1H, $H_1$), 4.24 (dd, 1H, $H_5$, $J_{4,5}$=5.4 Hz, $J_{5,6}$=3.4 Hz), 3.95 (d, 1H, $H_6$, $J_{5,6}$=3.4 Hz), 2.11 (s, 3H), 2.08 (s, 3H). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 171.7, 171.5, 90.3, 85.2, 74.9, 74.7, 51.8, 51.5, 22.3 (2C). IR (KBr) 3018, 1757, 1433, 1379, 1248, 1086, 1067, 1020, 916. Anal. calcd for $C_{10}H_{12}Br_2O_5$ (372.01): C, 32.29; H, 3.25; Found: C, 32.16, H, 3.23.

**4.1.9. Preparation of 2b from *endo*-diacetate 1.** To a solution of *endo*-diacetate **1** (1.00 g, 4.72 mmol) in $CH_2Cl_2$ (50 mL) were added 3 mL of AcBr and one drop $H_2SO_4$. The reaction mixture was stirred for 5 h at room temperature. The solvent and excess of AcBr were evaporated. The residue was dissolved in $CHCl_3$ and the solution filtered over an basic $Al_2O_3$ (Aktiv.1; 5 g). Removal of the solvent gave oily **2b**[4] (1.49 g, 94%).

**4.1.10. Preparation of 3b from *endo*-diacetate 1.** To a solution of *endo*-diacetate **1** (1.00 g, 4.72 mmol) in $CH_2Cl_2$ (50 mL) were added 3 mL of AcCl and one drop $H_2SO_4$. The reaction mixture was stirred for 12 h at room temperature. The solvent and excess of AcCl were evaporated. The residue was dissolved in $CHCl_3$ and the solution filtered over a basic $Al_2O_3$ (Aktiv.1; 5 g). Removal of the solvent gave oily **3b**[4] (1.07 g, 78%).

**4.1.11. Preparation of 2b from epoxide 5.** To a solution of epoxide **5** (0.80 g, 4.76 mmol) in 50 mL of $CH_2Cl_2$ was added a 3 mL of acetyl bromide. The reaction mixture was magnetically stirred at room temperature for 12 h. The solvent and excess of acetyl bromide were evaporated. The residue was dissolved in $CHCl_3$ and the solution filtered over an basic $Al_2O_3$ (Aktiv.1; 5 g). Removal of the solvent gave oily **2b**[4] (1.33 g, 83%).

**4.1.12. Preparation of 3b from epoxide 5.** The procedure

described in Section 4.1.11 was applied to epoxide **5** using AcCl to give oily **3b**[4] (85%).

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