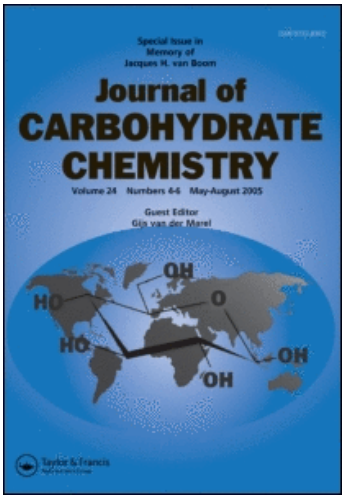

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CONTENTS

ABSTRACT

Regioselectivity in the reductive ring-opening reaction of 3,4,6-tri-*O*-benzyl-1,2-*O*-benzylidene and 3,4,6-tri-*O*-benzyl-1,2-*O*-*p*-methoxybenzylidene-α-D-glucopyranose using diisobutyl aluminum hydride (DIBAH) was examined. The ratio of the

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1-*O*- and 2-*O*-*p*-methoxybenzyl ethers, which were generated from endo-type 1,2-*O*-*p*-methoxybenzylidene, was variable by the change of solvent.

Key Words: Benzylidene; Acetal; Reduction; Ring-opening reaction; Protecting group.

INTRODUCTION

Benzylidene acetal, which can fix the ring conformation and react oxidatively or reductively, is a useful protective group in carbohydrate chemistry.[1,2] 4,6-*O*-Benzylidene aldohexopyranoses have been the most popular precursors, and numerous studies on the ring-opening reaction are known.[3] In the reaction of benzylidene acetal, the regioselectivity is dependent on a steric and/or an electronic factor.[4] However, the reaction of the 1,2-*O*-benzylidene derivatives linking the anomeric position is not yet well known. Very recently, an improved and practical synthesis of 1,2-*O*-benzylidene and 1,2-*O*-*p*-methoxybenzylidene hexopyranoses was reported, and a study on the regioselectivity in the reductive ring-opening reaction of 1,2-*O*-benzylidene and 1,2-*O*-*p*-methoxybenzylidene sugars was started.[5,6] The benzylidene sugar can generate two regiospecific benzyl ethers by the reductive ring-opening reactions.[7–16] However, the nature of the 1,2-*O*-benzylidene hexopyranoses, which differs from that of the 4,6-*O*-benzylidene hexopyranoses, is interesting. The ratio of the 1-*O*- and 2-*O*-benzyl ethers, which were obtained from the reductive ring-opening reaction of 1,2-*O*-benzylidene-α-D-glucopyranose, was variable by the conditions. This result prompted us to investigate reaction conditions for controlling the direction of this ring-opening (Fig. 1).

In this communication, we would like to report the reductive ring-opening reaction of 1,2-*O*-benzylidene and 1,2-*O*-*p*-methoxybenzylidene-α-D-glucopyranose using diisobutyl aluminum hydride (DIBAH).

RESULTS AND DISCUSSION

The acetal-bond cleavage of the 4,6-*O*-benzylidene and 4,6-*O*-*p*-methoxybenzylidene derivatives by the reaction with DIBAH is known,[17] and we applied it to 1,2-*O*-benzylidene and 1,2-*O*-*p*-methoxybenzylidene derivatives. In the reduction of benzylidene acetal, it has been known that the stereochemistry of the benzylidene position influences

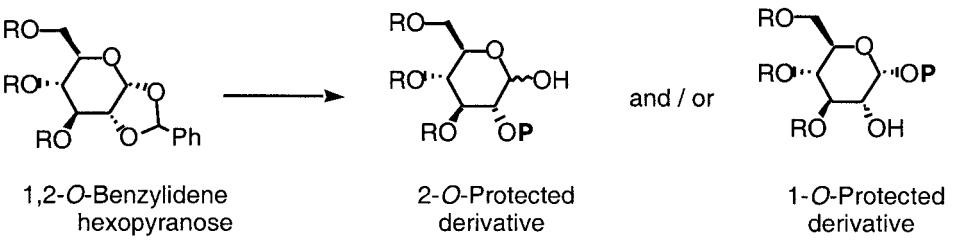
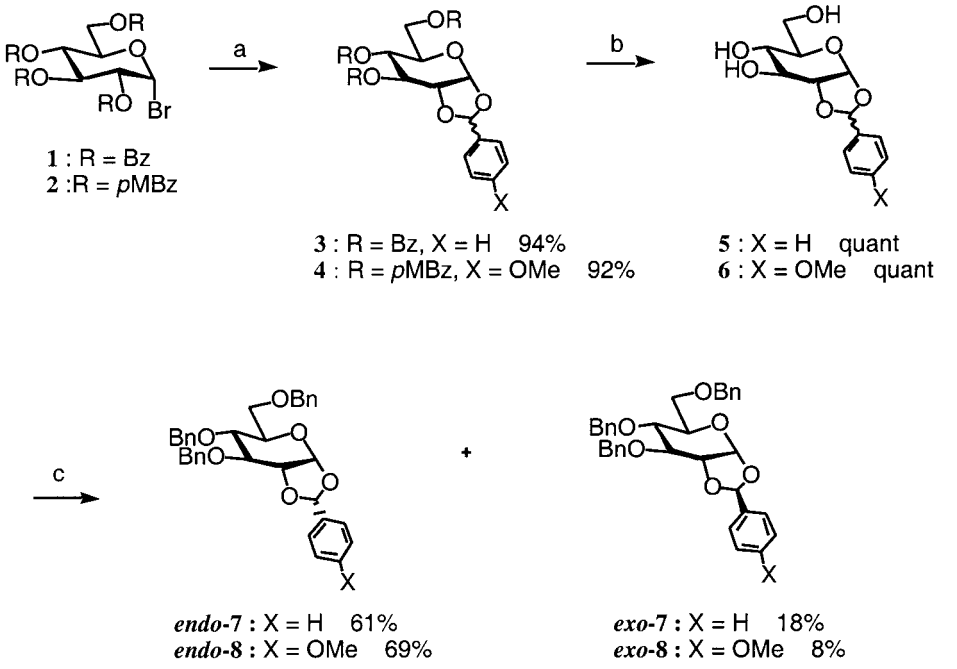


Figure 1. Reductive ring-opening reaction of 1,2-*O*-benzylidene-α-D-glucopyranose.



Scheme 1. Reagents and conditions: (a) $NaBH_4$, KI, MeCN; (b) NaOMe, MeOH; (c) BnBr, NaH, DMF.

the direction of ring-opening.[7,11] To compare the regioselectivity, endo- and exo-isomers of 1,2-*O*-benzylidene and 1,2-*O*-*p*-methoxybenzylidene-α-D-glucopyranoses (***endo*-7**, ***exo*-7**, ***endo*-8**, and ***exo*-8**) were prepared as shown in Sch. 1.

1,2-*O*-Benzylidene-α-D-glucopyranose **3** and 1,2-*O*-*p*-methoxybenzylidene-α-D-glucopyranose **4** were synthesized from the corresponding 2-*O*-benzoyl-glucopyranosyl bromide **1** or 2-*O*-*p*-methoxybenzoyl-glucopyranosyl bromide **2** by reductive cyclization.[5] Although the endo- and exo-isomers of **3** and **4** or 3,4,6-hydroxy-1,2-*O*-benzylidene **5** and 3,4,6-hydroxy-1,2-*O*-*p*-methoxybenzylidene **6** were difficult to separate, the corresponding 3,4,6-tri-*O*-benzyl derivatives were separable smoothly into the diastereomeric components by silica gel column chromatography. The structures of ***endo*-7**, ***exo*-7**, ***endo*-8**, and ***exo*-8** were confirmed by ^{1}H NMR.[a] The coupling constants

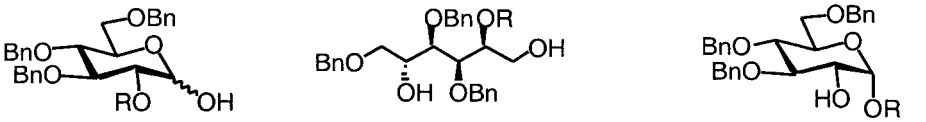
[a]Selected spectral data for 3,4,6-tri-*O*-benzyl-1,2-*O*-(*R*)-benzylidene-α-D-glucopyranose ***endo*-7**: $[\alpha]_D + 48.4^\circ$ (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) δ 7.54–7.16 (m, 20H, aromatic), 5.87 (s, 1H, benzylidene), 5.78 (d, 1H, $J_{1,2} = 5.5$ Hz, H-1), 4.72, 4.62, 4.59, 4.58, 4.48, 4.39 (each d, 6H, $J = 11.4$–12.1 Hz, benzyl), 4.30 (dd, 1H, $J_{2,3} = 3.7$ Hz, H-2), 4.04 (dt, 1H, $J_{4,5} = 9.5$, $J_{5,6a} = J_{5,6b} = 3.3$ Hz, H-5), 3.99 (dd, 1H, $J_{3,4} = 4.8$ Hz, H-3), 3.77 (dd, 1H, H-4), 3.67 (d, 2H, H-6a and 6b); 3,4,6-tri-*O*-benzyl-1,2-*O*-(*S*)-*p*-benzylidene-α-D-glucopyranose ***exo*-7**: $[\alpha]_D + 42.8^\circ$ (*c* 1.0, CH_2Cl_2); m.p.: 53–54°C (crystallized from EtOH); ^{1}H-NMR ($CDCl_3$) 7.46–7.26 (m, 20H, aromatic), 6.25 (s, 1H, benzylidene), 5.80 (d, 1H, $J_{1,2} = 4.8$ Hz, H-1), 4.79, 4.73, 4.66, 4.60, 4.52, 4.48 (each d, 6H, $J = 10.1$–12.5 Hz, benzyl), 4.36 (dd, 1H, $J_{2,3} = 4.8$ Hz, H-2), 3.97 (dd, 1H, $J_{3,4} = 6.2$ Hz, H-3), 3.93 (dt, 1H,

of $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ of both isomers were in good agreement with the known tri-*O*-acetate derivatives, respectively.[18] A NOE was observed between H-2 and the methine proton of the benzylidene group in the endo-isomers (***endo*-7** and ***endo*-8**). On the other hand, the exo-isomers (***exo*-7** and ***exo*-8**) showed a NOE between H-3 and the methine proton of the benzylidene group.

Isolated ***endo*-7**, ***exo*-7**, ***endo*-8** and ***exo*-8** were used in the reaction with DIBAH. Treatment of ***endo*-7**, ***exo*-7**, ***endo*-8**, or ***exo*-8** with DIBAH gave the corresponding ether, 2-*O*-Bn **9**[19] (or 2-*O*-Bn **10**) and 1-*O*-Bn **11** or 2-*O*-*p*MBn **12** and 1-*O*-*p*MBn **13** (Fig. 2). Results of the reductive ring-opening reaction are summarized in Table 1.

The ratio of 2-*O*-Bn **9** and 1-*O*-Bn **11**, which were generated from *endo*-type 1,2-*O*-benzylidene ***endo*-7**, was variable by the conditions. The change in regioselectivity by the solvent, temperature and reaction time was observed. In the reaction using CH_2Cl_2

$J_{4,5} = 9.5$, $J_{5,6a} = J_{5,6b} = 2.9$ Hz, H-5), 3.75 (dd, 1H, H-4), 3.71 (d, 2H, H-6a and 6b); 3,4,6-tri-*O*-benzyl-1,2-*O*-(*R*)-*p*-methoxybenzylidene-α-D-glucopyranose ***endo*-8**: $[\alpha]_D + 60.8^\circ$ (*c* 1.0, CH_2Cl_2); m.p.: 76–77°C (crystallized from EtOH); ^{1}H-NMR ($CDCl_3$) δ 7.45 (d, 2H, $J = 8.8$ Hz, aromatic), 7.35–7.17 (m, 15H, aromatic), 6.86 (d, 2H, $J = 8.8$ Hz, aromatic), 5.83 (s, 1H, benzylidene), 5.76 (d, 1H, $J_{1,2} = 5.1$ Hz, H-1), 4.71, 4.62, 4.59, 4.58, 4.49, 4.39 (each d, 6H, $J = 11.4$–12.5 Hz, benzyl), 4.28 (dd, 1H, $J_{2,3} = 4.4$ Hz, H-2), 4.06 (dt, 1H, $J_{4,5} = 9.5$, $J_{5,6a} = J_{5,6b} = 2.9$ Hz, H-5), 4.00 (dd, 1H, $J_{3,4} = 4.4$ Hz, H-3), 3.78 (s, 3H, OMe), 3.76 (dd, 1H, H-4), 3.68 (d, 2H, H-6a and 6b); 3,4,6-tri-*O*-benzyl-1,2-*O*-(*S*)-*p*-methoxybenzylidene-α-D-glucopyranose ***exo*-8**: $[\alpha]_D + 38.6^\circ$ (*c* 1.0, CH_2Cl_2); m.p.: 73–74°C (crystallized from EtOH); ^{1}H-NMR ($CDCl_3$) 7.38–7.20 (m, 17H, aromatic), 6.91 (d, 2H, $J = 8.8$ Hz, aromatic), 6.20 (s, 1H, benzylidene), 5.79 (d, 1H, $J_{1,2} = 5.1$ Hz, H-1), 4.80, 4.74, 4.67, 4.60, 4.51, 4.49 (each d, 6H, $J = 10.3$–12.1 Hz, benzyl), 4.37 (dd, 1H, $J_{2,3} = 5.1$ Hz, H-2), 3.95 (dd, 1H, $J_{3,4} = 6.2$ Hz, H-3), 3.91 (dt, 1H, $J_{4,5} = 9.5$, $J_{5,6a} = J_{5,6b} = 2.9$ Hz, H-5), 3.81 (s, 3H, OMe), 3.75 (dd, 1H, H-4), 3.71 (d, 2H, H-6a and 6b); 2,3,4,6-tetra-*O*-benzyl-α-D-glucitol **10**: $[\alpha]_D + 15.4^\circ$ (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) 7.41–7.21 (m, 20H, aromatic), 4.71, 4.67, 4.65, 4.62, 4.58, 4.55, 4.54, 4.50 (each d, 8H, $J = 11.4$–12.8 Hz, benzyl), 4.06–4.00 (m, 1H, H-5), 3.89 (dd, 1H, $J_{2,3} = 6.6$, $J_{3,4} = 3.7$ Hz, H-3), 3.82–3.53 (m, 6H, H-1a, 1b, 2, 4, 6a and 6b), 2.95 (d, 1H, $J_{5,\ OH} = 5.1$ Hz, OH), 2.10 (t, 1H, $J_{1a,OH} = 6.4$ Hz, OH); benzyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside **11**: $[\alpha]_D + 90.6^\circ$ (*c* 1.0, CH_2Cl_2); ^{1}H-NMR (CDCl3) 7.39–7.12 (m, 20H, aromatic), 5.03 (d, 1H, $J_{1,2} = 3.7$ Hz, H-1), 4.93, 4.83, 4.82, 4.75, 4.68, 4.54, 4.51, 4.48 (each d, 8H, $J = 9.9$–12.8 Hz, benzyl), 3.82 (ddd, 1H, $J_{4,5} = 9.9$, $J_{5,6a} = 3.3$, $J_{5,6b} = 1.8$ Hz, H-5), 3.79 (dd, 1H, $J_{2,3} = 9.9$ Hz, H-2), 3.74 (dd, 1H, $J_{3,4} = 8.8$ Hz, H-3), 3.74 (dd, 1H, $J_{6a,6b} = 10.6$ Hz, H-6a), 3.66 (dd, 1H, H-4), 3.62 (dd, 1H, H-6b), 2.13 (d, 1H, $J_{2,OH} = 8.4$ Hz, OH); 3,4,6-tri-*O*-benzyl- 2-*O*-*p*-methoxybenzyl-D-glucopyranose **12**: $[\alpha]_D + 40.0^\circ$ (*c* 0.6, CH_2Cl_2); mp: 122–123°C (crystallized from EtOH); ^{1}H-NMR ($CDCl_3$) δ 7.33–7.20, 7.14–7.10 and 6.83–6.79 (m, 19H, aromatic), 5.16 (br s, 0.8H, H-1α), 4.94–4.44 (m, 8.2H, benzyl and H-1β), 4.36 (d, 0.2H, $J_{1,OH} = 5.5$ Hz, OH), 4.03 (m, 0.8H, H-5α), 3.97 (t, 0.8H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3α), 3.74 (s, 2.4H, OMeα), 3.74 (s, 0.6H, OMeβ), 3.68 (d, 0.8H, $J_{1,OH} = 2.6$ Hz, OH), 3.66 (dd, 0.8H, $J_{5,6a} = 4.0$, $J_{6a,6b} = 9.9$ Hz, H-6aα), 3.66–3.46 (m, 1.8H, H-3β, 4β, 5β, 6aβ, 6bα and 6bβ), 3.38 (t, 0.2H, $J_{1,2} = J_{2,3} = 8.3$ Hz, H-2β); *p*-methoxybenzyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside **13**: $[\alpha]_D + 86.6^\circ$ (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) 7.37–7.21 (m, 15H, aromatic), 7.15–7.12 (m, 2H, aromatic), 6.87–6.85 (d, 2H, $J = 8.4$ Hz, aromatic), 4.99 (d, 1H, $J_{1,2} = 3.3$ Hz, H-1), 4.92, 4.81, 4.81, 4.67, 4.64, 4.51, 4.48, 4.47 (each d, 8H, $J = 10.6$–12.5 Hz, benzyl), 3.82 (ddd, 1H, $J_{4,5} = 9.9$, $J_{5,6a} = 3.3$, $J_{5,6b} = 1.5$ Hz, H-5), 3.77 (s, 3H, OMe), 3.79–3.75 (m, 2H, H-2 and 3), 3.74 (dd, 1H, $J_{6a,6b} = 10.6$ Hz, H-6a), 3.64 (dd, 1H, $J_{3,4} = 8.1$ Hz, H-4), 3.63 (dd, 1H, H-6b).



9 : R = Bn
12 : R = *p*MBn

10 : R = Bn

11 : R = Bn
13 : R = *p*MBn

Figure 2. Products of the ring-opening reactions.

or toluene as a solvent, the reaction smoothly proceeded to give 2-*O*-Bn **9** and 1-*O*-Bn **11** with the former preference (entry 1, 2). On the other hand, this reaction did not occur in the THF solution, and ***endo*-7** was recovered quantitatively (entry-3). It seems that DIBAH lost the reactivity to contact with *O*1 or *O*2 of ***endo*-7** by the Lewis basicity of THF. When the reaction was started at −78 to −20°C to control the reaction site, a reverse of the regioselectivity was observed (entry 4, 5). Under these conditions, the hemiacetal moiety of the product (2-*O*-Bn **9**) was reduced to the corresponding alditol (2-*O*-Bn **10**) because of the long reaction time. In this case, 2-*O*-Bn **10**, which must be transformed from the *O*1-aluminum complex *via* *O*5-aluminum complex, appeared within the time the starting compound ***endo*-7** remained. This result suggested that two types of the aluminum complex with the oxygen atoms, *O*1 and *O*2, of ***endo*-7** are estimated to exist as an

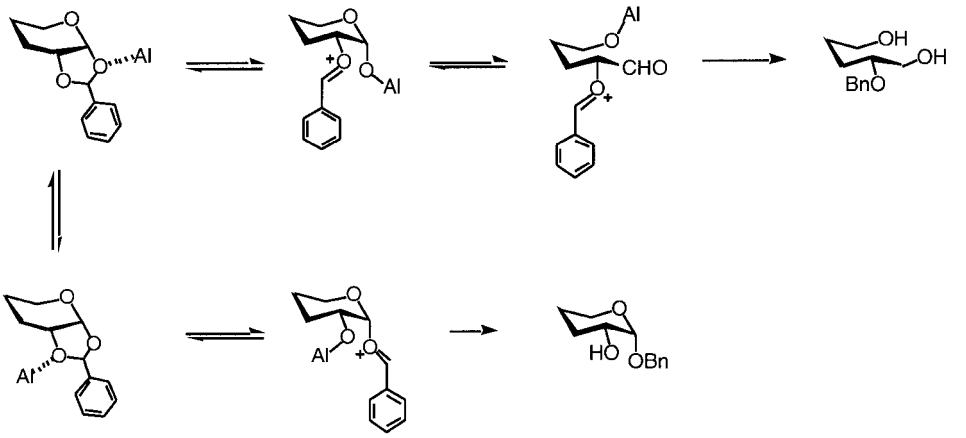
Table 1. Reductive ring-opening reactions of 1,2-*O*-benzylidene or 1,2-*O*-*p*-methoxybenzylidene-a-D-glucopyranose derivatives (***endo*-7**, ***endo*-8**, ***exo*-7**, and ***exo*-8**) with DIBAH.

Entry	Substrate	Temperature (°C)	Time	Solvent	Product (Yield %)[a]	
1	***endo*-7**	0	5 min	CH_2Cl_2	**9** (15)	**11** (85)
2	***endo*-7**	0	15 min	Toluene	**9** (30)	**11** (70)
3	***endo*-7**	−50 to reflux	5 hr	THF	—	—
4	***endo*-7**	−20 to 0	3 hr	CH_2Cl_2	**10** (75)	**11** (25)
5	***endo*-7**	−78 to 20	5 hr	CH_2Cl_2	**10** (89)	**11** (11)
6[b]	***endo*-7**	0 to 20	3 hr	CH_2Cl_2	**10** (72)	**11** (28)
7	***endo*-8**	−50	5 min	CH_2Cl_2	**12** (23)	**13** (77)
8	***endo*-8**	−50	15 min	Toluene	**12** (23)	**13** (77)
9	***endo*-8**	−78	15 min	CH_2Cl_2	**12** (18)	**13** (82)
10	***endo*-8**	−50 to −10	5 hr	THF	**12** (88)	**13** (12)
11	***exo*-7**	0	5 min	CH_2Cl_2	**9** (89)	**11** (11)
12	***exo*-7**	−78 to 20	15 min	CH_2Cl_2	**10** (100)	—
13	***exo*-8**	−78	15 min	CH_2Cl_2	**12** (100)	—
14	***exo*-8**	−50 to −10	5 hr	THF	**12** (100)	—

Note: These reaction were performed under the argon, atmosphere. Except for entry 6, the 1.0 M solution in toluene (10 eq.) was poured into the substrate solution (*ca.* 0.1 mmol/mL).

[a]The mixture of the products were recovered quantitatively and not isolated. The ratio of the products were determined by ^{1}H-NMR.

[b]The 1.0 M solution in toluene (3 eq.) was poured into the substrate solution (*ca.* 0.01 mmol/mL).



Scheme 2. An estimated equilibrium between the two aluminum complex of ***endo*-7**.

equilibrium state. Thus, the ratio of 1-*O*-Bn **11** and 2-*O*-Bn **10** may indicate that of the *O*2- and *O*1-aluminum complex. But, under the condition requiring long time to complete the ring-opening reaction, the *O*1-aluminum complex is consumed by generation of the corresponding alditol derivative (2-*O*-Bn **10**), and then is afforded by the equilibrium. As a result, the ratio of 1-*O*-Bn **11** to 2-*O*-Bn **10** decreased relatively (Sch. 2). This phenomenon was also observed in the reaction in the diluted solution (entry 6). The same tendency of the regioselectivity was observed in the reactions of ***endo*-8**. The reductive ring-opening reaction of ***endo*-8** in CH_2Cl_2 or toluene proceeded smoothly to give 2-*O*-*p*MBn **12** and 1-*O*-*p*MBn **13** with the former preference (entry 7–9). Based on the higher reactivity of ***endo*-8** than that of ***endo*-7**, this reaction occurred even in the THF solution (entry 10). Surprisingly, the ratio of 2-*O*-*p*MBn **12** and 1-*O*-*p*MBn **13** is dramatically inversed by the use of THF as a solvent. This result implies that the solvation of DIBAH is not advantageous for the formation of the *O*1-aluminum complex. At present, our research did not identify the factor controlling this reaction. But, the strict change of the reaction site with DIBAH is a matter of interest. Reaction of the *exo*-type substrates, ***exo*-7** and ***exo*-8**, gave the corresponding 2-*O*-Bn **9** or 2-*O*-*p*MBn **12** exclusively (entry 11–14). Interestingly, change of the solvent did not influence the regioselectivity in the reaction of the exo-isomer.

In summary, the procedure described herein offers a new option for the preparation of 1-*O*- or 2-*O*-benzyl type sugars, which are useful synthons for oligo-saccharide synthesis. To discuss the difference between endo- and exo-type substrates in the reaction with DIBAH, more examination, such as from the viewpoint of the stereoelectronic effect, including conformational studies, is currently under way.

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