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Reductive Ring-Opening Reaction of 1,2-O-Benzylidene and 1,2-O-p-Methoxybenzylidene-a-D-glucopyrar Using Diisobutyl Aluminum Hydride

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Reductive Ring-Opening Reaction of 1,2-*O*-**Benzylidene and 1,2-***O*-*p*-**Methoxybenzylidene-α-**D**glucopyranose Using Diisobutyl Aluminum Hydride**

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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*-benzy-lidene 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) NaBH₄, 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 ¹H NMR.^a The coupling constants

^aSelected spectral data for 3,4,6-tri-*O*-benzyl-1,2-*O*-(*R*)-benzylidene- α -D-glucopyranose *endo*-7: $[\alpha]_{\rm D}$ + 48.4° (*c* 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃) 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: $[\alpha]_{\rm D}$ + 42.8° (*c* 1.0, CH₂Cl₂); m.p.: 53–54°C (crystallized from EtOH); ¹H-NMR (CDCl₃) 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-Obenzyl-1,2-O-(R)-p-methoxybenzylidene- α -D-glucopyranose **endo-8**: $[\alpha]_D + 60.8^{\circ}$ (c 1.0, CH₂Cl₂); m.p.: 76–77°C (crystallized from EtOH); ¹H-NMR (CDCl₃) 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**: $[\alpha]_{\rm D} + 38.6^{\circ}$ (c 1.0, CH₂Cl₂); m.p.: 73–74°C (crystallized from EtOH); ¹H-NMR (CDCl₃) 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° (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃) 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 = 11.4-12.8Hz, 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, CH₂Cl₂); ¹H-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-4), 3.62 (dd, 1H, H-4), 3.62 (dd, 1H, H-4), 3.62 (dd, 1H, H-4), 3.63 (dd, 1H, H-4), 3.63 (dd, 1H, H-4), 3.63 (dd, 1H, H-4), 3.63 (dd, 1H, H-4), 3.64 (dd, 1H, H-4), 3.64 (dd, 1H, H-4), 3.65 (dd, 1H, H 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**: $[\alpha]_{\rm D} + 40.0^{\circ}$ (*c* 0.6, CH₂Cl₂); mp: 122–123°C (crystallized from EtOH); ¹H-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-1 α), 4.94–4.44 (m, 8.2H, benzyl and H-1 β), 4.36 (d, 0.2H, $J_{1,OH} = 5.5$ Hz, OH), 4.03 (m, 0.8H, H-5 α), 3.97 (t, 0.8H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3 α), 3.74 (s, 2.4H, OMe α), 3.74 (s, 0.6H, OMe β), 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-6a α), 3.66– 3.46 (m, 1.8H, H-3 β , 4 β , 5 β , 6a β , 6b α and 6b β), 3.38 (t, 0.2H, $J_{1,2} = J_{2,3} = 8.3$ Hz, H-2 β); *p*-methoxybenzyl 3,4,6-tri-O-benzyl- α -D-glucopyranoside **13**: $[\alpha]_{\rm D} + 86.6^{\circ}$ (c 1.0, CH₂Cl₂); ¹H-NMR (CDCl₃) 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).



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

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)	—

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

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).

^aThe mixture of the products were recovered quantitatively and not isolated. The ratio of the products were determined by ¹H-NMR.

^bThe 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 O2- and O1-aluminum complex. But, under the condition requiring long time to complete the ring-opening reaction, the O1-aluminum complex is consumed by generation of the corresponding additol 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 CH₂Cl₂ or toluene proceeded smoothly to give 2-O-pMBn 12 and 1-O-pMBn 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-pMBn 12 and 1-O-pMBn 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 O1-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-pMBn 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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