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Preparation of methyl 4,6-di-*O*-acetyl-3-*C*-nitro-2-enopyranoside derivatives and their reduction with sodium borodeuteride

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Abstract

The conformationally flexible title compounds were prepared and subjected to reduction with sodium borodeuteride. Deuteride ion attacks exclusively from the side opposite of the anomeric methoxyl group. However, the stereoselectivity of a similar reduction of the corresponding 4,6-*O*-benzylidene-β-D-*threo*-2-enopyranoside derivative, adopting the $^{0}H_{5}$ conformation, was exceptionally low, suggesting that reduction of the 4,6-diacetate having the β-D-*threo* configuration did not occur from the stable $^{0}H_{5}$ conformation, but from an unstable ($^{5}H_{0}$) one.

Keywords: Cyclic nitroalkenes; Stereochemistry of reduction; Conformation

1. Introduction

The stereoselectivities of addition reactions to unsaturated sugars are of current interest, and many efforts have been made to determine the factors controlling the direction of approach of a nucleophile. We have studied nucleophilic additions to conformationally rigid 2-enopyranoside derivatives having an electron-withdrawing group at C-2 or C-3 [1] and have proposed three factors for explaining the stereoselectivities observed [2].

Here we report the preparation, structure determination, and reactions with sodium

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borodeuteride of conformationally flexible, 4,6-diacetates having the α-D-*erythro*, β-D-*erythro*, α-D-*threo*, and β-D-*threo* configurations (**4**, **6**, **10**, and **12**).

2. Results and discussion

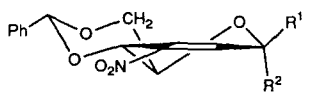
The β-D-*erythro* (**6**), α-D-*threo* (**10**), and β-D-*threo*-2-enopyranosides (**12**) were prepared from the corresponding 4,6-*O*-benzylidene derivatives **2**, **7**, and **8**, respectively, according to the method described for the preparation of the α-D-*erythro*-2-enopyranoside **4** [3]. The structures **1–29** are shown in Scheme 1.

Conformation of the 3-nitro-2-enopyranosides.—The conformations of the dihydroxy derivatives **3**, **9**, and **11** as well as the 4,6-diacetates **4**, **6**, **10**, and **12** were determined by ^{1}H NMR spectroscopy (Table 1). On the basis of the $J_{4,5}$ [4] and $^1J_{C\text{-}1,H\text{-}1}$ values [1], the $^0H_5$ conformation was assigned to the α-D-*erythro* isomers **3** and **4**, and the $^5H_0$ conformation to the 4,6-di-*O*-acetyl-β-D-2-enopyranoside **6**. Long-range allylic coupling ($^2J_{2,4}$) with the quasiaxial proton amounts to 1.0–1.3 Hz, whereas that with the quasiequatorial proton is negligible [6]. The allylic coupling values did not conflict with these assignments. The 4,6-dihydroxy derivative of the β-D-*erythro* isomer **5** seems to be an equilibrium mixture of the $^0H_5$ and $^5H_0$ conformations according to the $J_{4,5}$ value (5.0 Hz): this was significantly different from those for the diacetate **6** (1.7 Hz) and 4,6-*O*-benzylidene derivative **2** (8.2 Hz). Although the $^1J_{C\text{-}1,H\text{-}1}$ value (165 Hz) of **5** is the same as that of the 4,6-*O*-benzylidene derivative **2**, a long-range allylic coupling ($^2J_{2,4}$) was not observed in **5**, in contrast to the case for **2** ($^2J_{2,4}$ 1.9 Hz). The $J_{4,5}$ values were not conformationally diagnostic for the *threo* isomers **10** and **12**, because the dihedral angle between H-4 and H-5 in the $^0H_5$ conformer is almost the same as that for the $^5H_0$ one, as judged from stereo models. The $J_{1,2}$ and $J_{4,5}$ coupling constants of **9**, **10**, **11**, and **12** are in good agreement with those of the corresponding 4,6-*O*-benzylidene derivatives **7** and **8** [2], respectively, suggesting that these compounds have the $^0H_5$ conformation. This speculation was supported by the $^2J_{2,4}$ (0 Hz) and $^1J_{C\text{-}1,H\text{-}1}$ values (see Tables 2 and 3). In the case of the β-D anomer **12**, the $^0H_5$ conformation was confirmed by the NOE difference spectrum. The H-1 signals were enhanced (12%) by irradiation at the H-5 resonance, indicating that H-1 and H-5 are in 1,3-diaxial relationship.

The conformations of these nitroalkenes appear to be controlled mainly by the following three factors: (*i*) the $A^{(1,2)}$ strain between the nitro group and the acetoxyl

[1] It is conceivable that the $^1J_{C\text{-}1,H\text{-}1}$ value of a 2-enopyranoside derivative deviates from the standard values derived from saturated pyranosides, because an aglycon in the former occupies the quasiaxial or quasiequatorial position. In fact compounds **1** and **2** had $^1J_{C\text{-}1,H\text{-}1}$ values of 170 and 165 Hz, respectively. The former is in good agreement with standard values for compounds having an axial aglycon, whereas the latter is larger by 5 Hz than for standard compounds having an equatorial aglycon [5]. Therefore, if the $^1J_{C\text{-}1,H\text{-}1}$ value of a 3-*C*-nitro-2-enopyranoside is larger than 168 or smaller than 165 Hz, we assume that it may have the methoxyl group quasiaxial or quasiequatorial, respectively.

[2] The $^0H_5$ conformation for **8** was confirmed by the NOE difference spectrum: H-1 enhancement (10%) was observed upon irradiation at the H-5 resonance.



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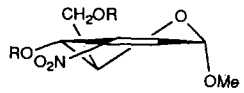
2 R^1 = OMe, R^2 = H



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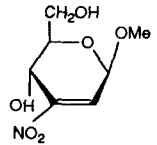
4 R = Ac



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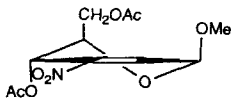

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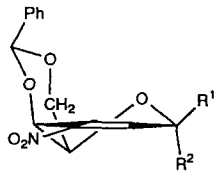
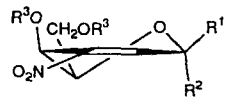
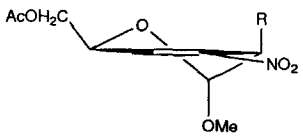


7 R^1 = H, R^2 = OMe
8 R^1 = OMe, R^2 = H



9 R^1 = R^3 = H, R^2 = OMe
10 R^1 = H, R^2 = OMe, R^3 = Ac
11 R^1 = OMe, R^2 = R^3 = H
12 R^1 = OMe, R^2 = H, R^3 = Ac



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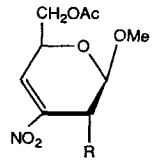
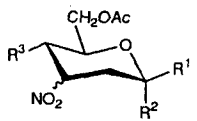
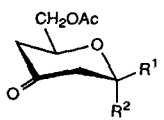
14 R = D



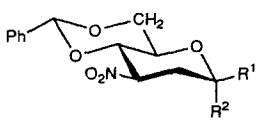
15 R = H
16 R = D



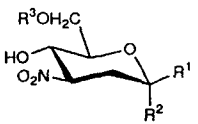
17 R^1 = R^3 = H, R^2 = OMe
18 R^1 = H, R^2 = OMe, R^3 = OAc
19 R^1 = OMe, R^2 = H, R^3 = OAc



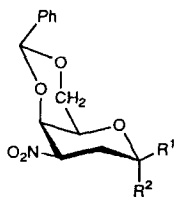
20 R^1 = H, R^2 = OMe
21 R^1 = OMe, R^2 = H



22 R^1 = H, R^2 = OMe
23 R^1 = OMe, R^2 = H



24 R^1 = R^3 = H, R^2 = OMe,
25 R^1 = H, R^2 = OMe, R^3 = Ac
26 R^1 = OMe, R^2 = R^3 = H
27 R^1 = OMe, R^2 = H, R^3 = Ac



28 R^1 = H, R^2 = OMe
29 R^1 = OMe, R^2 = H

Table 1
^{1}H NMR chemical shifts (δ, ppm) [a]

Compound	H-1	H-2a	H-2e	H-3	H-4	H-5	H-6	H-6′	OMe	OAc	Other signals
5	5.34 (dd)	7.12 (d)		–	4.84 (br s)		3.8–4.0 (m)		3.57 (s)	–	3.19 (br s [b], 4-OH)
6 [c]	4.57 (d)	6.78 (d)		–	6.13 (d)	4.33 (ddd)	4.23 (dd)	4.06 (dd)	2.99 (s)	1.78 (s)	1.51 (s,OAc)
9 [d]	5.29 (d)	7.16 (d)		–	4.61 (d)	3.97 (ddd)	3.75–3.85 (m)		3.48 (s)		
10	5.33 (d)	7.35 (d)		–	6.02 (d)	4.37 (ddd)	4.30 (dd)	4.17 (dd)	3.51 (s)	2.09 (s)	2.10 (OAc)
11	5.29 (t)	7.17 (d)		–	4.75 (ddd)	3.81 (ddd)	4.04 (dd)	3.95 (dd)	3.59 (s)		2.84 (d, 4-OH); 2.13 (brs, 6-OH)
12	5.32 (t)	7.33 (d)		–	6.11 (dd)	4.04 (dt)	4.19 (dd)	4.29 (dd)	3.60 (s)	2.10 (s)	2.12 (s, OAc)
13	5.13 (br d)	2.87 (br dtd)	2.75 (br dd)	–	7.21 (br s)	4.59 (dddd)	4.37 (dd)	4.27 (dd)	3.45 (s)	2.11 (s)	
15	4.80 (dd)	2.73 (dddd)	2.91 (ddt)	–	7.23 (dd)	4.68 (dtd)	4.36 (dd)	4.23 (dd)	3.52 (s)	2.12 (s)	
20 [c]	4.58 (dd)	2.04 (ddd)	2.31 (br dt)	–	–		3.84–3.95 (m)		2.98 (s)	1.68 (s)	1.92 (br dd, H-4a); 2.07 (ddd, H-4e)
21	4.68 (dd)	2.50 (dd)	2.69 (ddd)	–	–	3.96 (tdd)	4.21 (dd)	4.26 (dd)	3.54 (s)	2.11 (s)	2.47 (dd, H-4a); 2.38 (ddd, H-4e)
24	4.88 (dd)	2.14 (dt)	2.48 (ddd)	4.84 (ddd)	4.23 (t)	3.67 (dt)	3.91 (t)	3.37 (s)			
25 [e]	4.89 (s)	2.44 (d)	4.82 (dd)	3.99 (dt)	3.77 (ddd)	4.60 (dd)	4.25 (dd)	3.37 (s)	2.16 (s)		3.41(d, OH)
26 [d]	4.55 (dd)	1.95 (td)	2.40 (ddd)	4.69 (ddd)	3.94 (t)	3.32 (ddd)	3.86 (dd)	3.73 (dd)	3.48 (s)		
27	4.49 (dd)	2.08 (td)	2.54 (ddd)	4.56 (ddd)	4.00 (dt)	3.46 (ddd)	4.63 (dd)	4.28 (dd)	3.52 (s)	2.17 (s)	3.30 (d, OH)
28	5.06 (br dd)	2.63 (td)	2.26 (br dd)	4.88 (ddd)	4.76 (d)	3.73 (br d)	4.33 (dd)	4.15 (dd)	3.40 (s)		5.63 (s, PhCH)
29	4.45 (dd)	2.51 (td)	2.32 (ddd)	4.57 (ddd)	4.67 (br d)	3.49 (br t)	4.39 (dd)	4.15 (dd)	3.55 (s)		5.11 (s, PhCH)

[a] 270 MHz in $CDCl_3$ (otherwise cited).
[b] H-4 signal became doublet by addition of D_2O.
[c] In C_6D_6.
[d] In CD_3OD.
[e] C-2 axially monodeuterated derivative of **25**.

group at C-4 [7] [3], (*ii*) the anomeric effect [10], and (*iii*) the predominant equatorial disposition of the hydroxymethyl or acetoxymethyl group at C-5. The $^5H_0$ conformation is favored in the *β*-D-*erythro* isomer **6** because of factors (*i*) and (*ii*), but disfavored

[3] This factor, indicating that the acetoxyl group at C-4 should occupy the quasiaxial position, might be enhanced, because the quasiaxial orientation of the acetoxyl group is more favorable than the alternative one by 0.45 kcal/mol in the case of 1-acetoxy-2-cyclohexene [8]. The important roles of the $A^{(1,2)}$ strain and the $A^{(1,3)}$ strain for stability and reactivity in nitro sugars are discussed by Baer et al. [9].

Table 2
^{1}H NMR coupling constants (Hz) [a]

Compound	$J_{1,2a}$	$J_{1,2e}$	$J_{2a,2e}$	$J_{2a,3}$	$J_{2e,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	Other couplings
5 [b]		2.0	–	–	–	–	5.0				1.3 ($J_{1,4}$)
6 [c]		3.0	–	–	–	–	1.7	5.6	7.9	11.6	
9 [d]		3.0	–	–	–	–	2.0	5.3	7.3		
10		3.3	–	–	–	–	2.3	5.0	7.3	11.6	
11		1.3	–	–	–	–	2.3	5.3	7.6	11.9	1.3 ($J_{1,4}$); 6.3 ($J_{4,OH}$)
12		1.0	–	–	–	–	2.3	6.9	6.3	11.6	1.0 ($J_{1,4}$)
13	4.3	~0.7	17.8	–	–	–		5.3	5.0	11.6	2.0 ($J_{2a,4}$); 4.3 ($J_{2a,5}$); 3.3 ($J_{2e,5}$)
15	5.8	3.8	17.5	–	–	–	3.6	6.3	6.0	11.3	1.7 ($J_{2a,4}$); 3.0 ($J_{2a,5}$); 1.5 ($J_{2e,4}$); 3.3 ($J_{2e,5}$)
20 [c]	4.6	1.3	14.8	–	–	–					0.7 ($J_{2a,4a}$); 2.0 ($J_{2e,4e}$); ~14 ($J_{4a,4e}$); 10.2 ($J_{4a,5}$); 3.0 ($J_{4e,5}$)
21	7.9	3.0	15.5	–	–	–		4.3	5.3	11.9	1.3 ($J_{2e,4e}$); 15.5 ($J_{4a,4e}$); 10.6 ($J_{4a,5}$); 4.0 ($J_{4e,5}$)
24	3.6	1.3	12.9	12.9	4.9	9.9	9.6	3.3	3.3		
25 [e]		~0	–		4.3	9.6	9.9	3.6	2.3	12.5	2.3 ($J_{4,OH}$)
26 [d]	9.6	2.0	12.2	12.9	4.6	9.6	9.9	2.3	5.3	11.9	
27	9.6	2.3	12.9	12.9	5.0	9.6	9.8	3.6	2.3	12.5	4.3 ($J_{4,OH}$)
28	3.4	~1.0	12.8	12.8	4.5	3.5	~1.0	1.7	1.7	12.5	~0.8 ($J_{1,5}$)
29	9.6	2.0	12.5	12.5	4.3	3.7	~0	1.6	1.8	12.5	

[a] 270 MHz in $CDCl_3$ (otherwise cited).
[b] H-4 signal became doublet by addition of D_2O.
[c] In C_6D_6.
[d] In CD_3OD.
[e] C-2 axially monodeuterated derivative of **25**.

Table 3
^{13}C NMR chemical shifts (δ, ppm) and $^1J_{C\text{-}1,H\text{-}1}$ data (Hz) [a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	OMe	$^1J_{C\text{-}1,H\text{-}1}$
3 [b]	94.9	129.3		61.7	71.4	61.6	56.7	169
4 [b]	94.4	131.0	148.6	61.6	68.2	62.1	56.6	170
5	96.1	130.9	151.0	61.0	77.7	62.7	56.7	165
6	94.6	132.4	145.6	61.3	73.9	62.5	56.7	169
9	96.2	131.5	153.0	61.4	74.0	62.3	56.8	169
10	94.3	132.6	147.3	60.3	68.3	61.7	56.5	170
11	97.6	133.1		61.8	75.3	61.7	56.5	161
12	97.3	135.3	147.7	60.7	72.3	61.5	56.5	161
13	96.7	29.4	146.8	129.6	65.5	64.2	55.3	170
15	98.6	29.8	146.0	129.9	69.9	64.5	56.3	164
21	100.8	47.2	204.2	42.6	69.3	65.7	56.3	

[a] 67.8 MHz in $CDCl_3$.
[b] These compounds were prepared in the previous paper [3]. Additional data.

because of factor (*iii*). Compound **6** adopts the $^5H_0$ conformation, indicating that a sum of factors (*i*) and (*ii*) overwhelms the 1,3-diaxial repulsion between the acetoxymethyl and methoxyl groups (factor (*iii*)). A summation of factors (*i*) and (*iii*) overcomes factor (*ii*), as illustrated in the β-D-*threo* isomer **12**, which assumes the $^0H_5$ conformation. The α-D-*erythro* isomer **4** exists in the $^0H_5$ conformation, indicating that factors (*ii*) plus (*iii*) play a more important role than factor (*i*) only. Thus the present study suggests that the sum of any two factors surpasses the remaining one factor. If hydrogen bonding operates between the hydroxyl group at C-4 and the nitro group at C-3, the disadvantage due to factor (*i*) is reduced or reversed. If this is so, it is understandable that the 4,6-dihydroxy derivative **5** equilibrates between the $^5H_0$ and $^0H_5$ conformations. Thus all diacetates take the same conformation ($^0H_5$) as the corresponding 4,6-*O*-benzylidene derivatives, except for **6**.

Reductions.—It is well known that the S_N2' process occurs in nucleophilic addition-reactions to nitroalkenes having a leaving group at the β′ position [11]. We examined the reactions of 2-enopyranosides **4**, **6**, **10**, and **12** with sodium borohydride. Phase-transfer catalyzed reduction of the α-D-*erythro* isomer **4** with sodium borohydride gave two major products, along with the unreacted starting nitroalkene **4**, as judged by ^{1}H NMR spectroscopy, which indicated that one product (**13**) was converted into the other one (**17**). Compound **13** has a nitroalkene moiety (1520 cm^{-1}), whereas **17** has a saturated nitro group (1560 cm^{-1}), indicating that the double bond of the S_N2' product **13** was further reduced to **17**. Under suitable conditions, the 3-enopyranoside **13** could be isolated in 73% yield. In order to isolate **17**, a large excess of sodium borohydride was employed in methanolic solution, and the reaction mixture was simply evaporated without washing. The spectral data of the resulting residue suggested that it was a 3-epimeric mixture of nitro compounds (probably the *threo* isomer, along with a small amount of *erythro* [4]), but separation was unsuccessful, because the products partially decomposed during column chromatography on silica gel and preparative TLC. However, when the reaction mixture was washed with dilute aq hydrochloric acid, the glycos-3-ulose **20** was obtained in 78% yield. Similar results were observed in the case of the β-D-*erythro* isomer **6**, which gave the glycos-3-ulose **21** in 72% yield.

Reduction of the β-D-*erythro* isomer **6** with sodium borohydride afforded the corresponding 3-enopyranoside **15** in 81% yield. No evidence for the formation of simple adducts, **18** and **19**, was obtained in these reductions.

The α-D-3-enopyranoside **13** was assigned the $^0H_1$ conformation from the $J_{1,2a}$ (4.3 Hz), $J_{2a,4}$ (2.0 Hz), and $^1J_{C\text{-}1,H\text{-}1}$ values (170 Hz). In contrast, the β-D-3-enopyranoside **15** seems to be an equilibrium mixture of the $^0H_1$ and $^1H_0$ conformations, with the former being more important, as judged from the $J_{1,2a}$ (5.8 Hz), $J_{2a,4}$ (1.7 Hz), $J_{2e,4}$ (1.5 Hz), $^1J_{C\text{-}1,H\text{-}1}$ values (164 Hz), and the NOE difference spectrum. Irradiation at the H-1 and H-5 resonance enhanced the H-5 (6%) and H-1 (7%) signals, respectively.

[4] Partial ^{1}H NMR data for the major product: 4.97 (br d, 1 H, $J_{1,2a}$ 2.5 Hz, H-1), 4.87 (tt, 1 H, $J_{2a,3} = J_{3,4a} = 12.2$, $J_{2e,3} = J_{3,4e} = 4.3$ Hz, H-3); for the minor one: 4.79 (br d, 1 H, $J_{1,2a}$ 3.6 Hz, H-1), 4.54 (dt, $J_{2a,3}$ 5.7, $J_{2e,3} = J_{3,4e} = 2.0$, $J_{3,4a}$ 4.4 Hz, H-3).

Reduction of the α-D-*erythro* isomer **4** with sodium borodeuteride afforded the α-D-3-enopyranoside **14** in 65% yield [5]. Attack by a deuteride ion from the upper side was chemically confirmed as follows. The monodeuterio derivative of the 4,6-*O*-benzylidene derivative **22** [12,13], in which the deuterium atom had been introduced at the C-2 axial position [14], was debenzylidenated to the 2-deuterio derivative of **24**, and then acetylated selectively at C-6 to give the deuterio derivative of **25**. Mesylation followed by elimination of methanesulfonic acid gave the 3-enopyranoside, identical with **14** by ^{1}H NMR spectroscopy. The β-D-*erythro* anomer **6** was similarly reduced with sodium borodeuteride to give the β-D-3-enopyranoside **16** in 70% yield[5]. In this reaction a deuteride ion attacked from the same side as the leaving group, in contrast to the case of the α-D-anomer **4**: this was again confirmed by conversion of the deuterio derivative of **23** at the C-2 equatorial position via the deuterio derivatives of the dihydroxy derivative **26** and the 6-acetate **27**. Reductions of the *threo* isomers **10** and **12** with sodium borodeuteride afforded the α-D- **14** and β-D-3-enopyranoside **16** in 55% and 63% yields[5], respectively; here a deuteride ion added exclusively from the upper side of the α-D-*threo* isomer **10** and from the lower side of the β-D-*threo* isomer **12**.

As already reported [14], sodium borodeuteride added exclusively in the *trans* manner to the anomeric methoxyl group in the case of the 4,6-*O*-benzylidene-α-D-*erythro* isomer **1** and its β anomer **2**. However, reduction of the corresponding 4,6-*O*-benzylidene derivatives having the *threo* configurations (**7** and **8**) has not yet been investigated. Reduction of the α-D-*threo* isomer **7** gave a 5:1 mixture of axially and equatorially deuterated derivatives of **28** in 99% yield. Similar reduction of the β-D-*threo* isomer **8** showed a low stereoselectivity, affording a 1:1.7 mixture of axially and equatorially deuterated derivatives of **29** in 74% yield.

Stereoselectivities of the reductions.—The results indicate high selectivity for attack by a deuteride ion at the C-2 position of all substrates, from the opposite side of the anomeric methoxyl group, except for the case of the 4,6-*O*-benzylidene-β-D-*threo* isomer **8**. A similar bias is observed in the epoxidation of 4,6-*O*-benzylidene derivatives with hydrogen peroxide [15], where the β-D-*threo* isomer **8** showed low stereoselectivity as compared with other substrates. Undoubtedly reduction of 4,6-*O*-benzylidene derivatives proceeds via a nitronate. However, two reaction routes have been proposed for the S_N2' reaction: one is a concerted one-step mechanism and the other is a stepwise one involving a nitronate (Fig. 1) [11]. If the S_N2' reaction occurred by the former mechanism, a nucleophile would add preferentially from the same side of the leaving group (*syn* addition) [16]. However, even in the concerted mechanism, Toromanoff [17] speculated that if a leaving group occupies the quasiequatorial position, a nucleophile adds in the *anti* manner to the leaving group, in conflict with the case of quasiaxial disposition of the leaving group. Therefore, the different stereoselectivities observed between the 4,6-*O*-benzylidene derivative **8** and the 4,6-diacetate **12** seem to be explained in terms of (*1*) the reactive conformers are different from each other, and/or

[5] The stereoselectivity should be high, because the 3-enopyranosides isolated were pure by ^{1}H NMR spectroscopy. The moderate yields of **14** (from **4** and **10**) and **16** (from **6** and **12**) might be a result of overreduction.

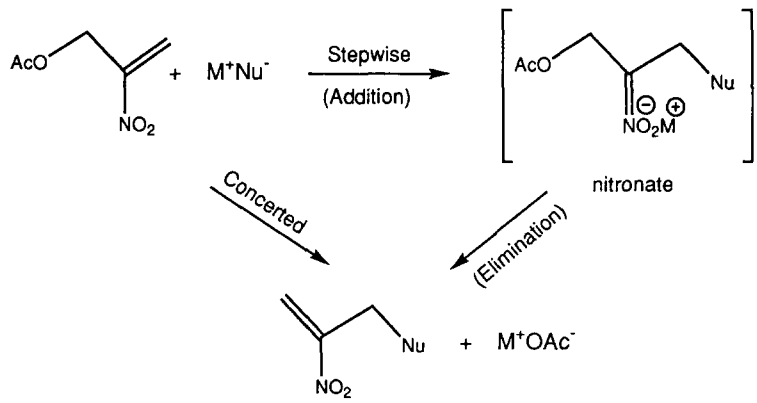


Fig. 1. Two types of reaction mechanism for S_N2' reaction.

(2) the reaction of the 4,6-diacetate **12** proceeds by the concerted one-step (S_N2') mechanism. However, the latter possibility appears low, because the stereoselectivities of 4,6-*O*-benzylidene derivatives and the corresponding acetates were almost the same, except for the β-D-*threo* isomers. Furthermore, as reported in previous papers [3,18], the S_N2' reaction of the acetate **4** with *tert*-butyl hydroperoxide appears to proceed via a nitronate. Thus the former possibility is high. If these β-D-*threo* isomers react through the $^0H_5$ conformation, a nucleophile approaches from the upper side owing to stereoelectronic control [6] as well as the $A^{(1,3)}$ strain [7], while it comes from the lower side to avoid steric and electrostatic repulsion arising from the anomeric methoxyl group and the oxygen atom at O-4 (Fig. 2). Experimental results suggest that the latter repulsion plays a more important role than the former two factors. Such a steric and electrostatic repulsion should be enhanced in the $^5H_0$ conformation, because in this conformation the anomeric methoxyl group occupies the more-crowded quasiaxial position. Furthermore, in the $^5H_0$ conformation, attack from the axial side is favored by stereoelectronic control. Therefore, the exclusive attack of a deuteride ion from the lower side of the 4,6-diacetate **12** strongly suggests that the reduction proceeds via the $^5H_0$ conformation, whereas the low stereoselectivity observed in the 4,6-*O*-benzylidene derivative **8** suggests that the reaction occurs from the $^0H_5$ conformation. This conclusion is likely, because the inversion of the $^0H_5$ conformation into the $^5H_0$ one probably occurs more smoothly in the 4,6-diacetate **12** than in the 4,6-*O*-benzylidene derivative **8**.

Thus the reductions of **8** and **12** having the β-D-*threo* structures appear to give useful information about a reactive conformer, whereas those of the β-D-*erythro* isomers, **2** and **6**, do not. If reduction of the β-D-*erythro* isomer **6** proceeded through the most stable

[6] If a nucleophile approaches from the axial side (upper and lower side in the $^0H_5$ and $^5H_0$ conformations, respectively), an intermediary nitronate would have a more-stable chair structure owing to stereoelectronic control [19], whereas alternative attack leads to a less-stable boat structure.

[7] If stereoelectronic control operates, a nucleophile should attack from the same side of a substituent at the β′ position (the substituent at C-4 in the present substrates) to avoid the $A^{(1,3)}$ strain [7] between the nitronate and the β′ substituent.

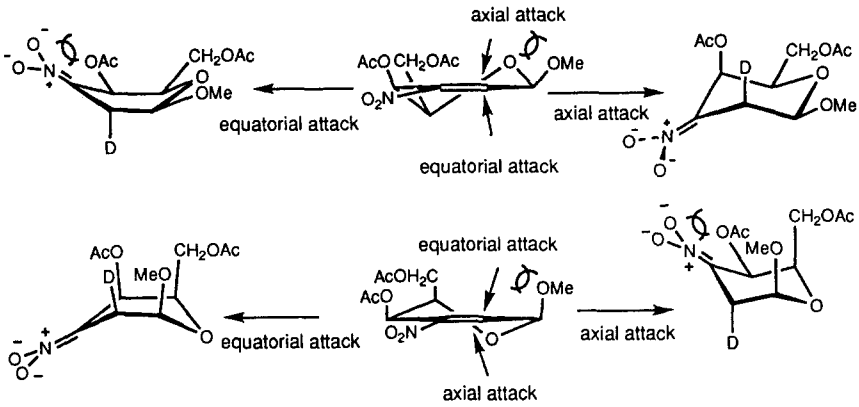


Fig. 2. Intermediary nitronate formed by axial and equatorial attack.

$^5H_0$ conformation, a deuteride ion approaches from the lower side (axial attack) because of $A^{(1,3)}$ strain, stereoelectronic control, and steric and electrostatic repulsion owing to the methoxyl group. However, the same stereoselectivity must be observed even if the reduction proceeds through the $^0H_5$ conformation, because a deuteride ion approaches exclusively from the lower side of the 4,6-*O*-benzylidene derivative **2** having the $^0H_5$ conformation [14].

3. Experimental

General methods.—Melting points are uncorrected. Optical rotations were determined with a Horiba High Sensitivity Polarimeter (SEPA-200). ^{1}H and ^{13}C NMR spectra were recorded at 270 and 67.8 MHz, respectively, with a spectrometer (JNM-EX270) in $CDCl_3$ with Me_4Si as the internal standard (unless otherwise cited). The integration values in the NOE difference spectra are estimated only roughly, because measurement conditions were not completely optimized. IR spectra were recorded for KBr pellets. Reaction mixtures were dried over $MgSO_4$ and evaporated under diminished pressure. Column chromatography was conducted on silica gel (Wakogel C-300). The catalyst used refers to hexadecyltributylphosphonium bromide.

*Methyl 2,3-dideoxy-3-*C*-nitro-β-*D*-*erythro*-hex-2-enopyranoside* (**5**).—A dispersion of **2** [20] (10 g, 34.1 mmol) in 90% aq AcOH (100 mL) was heated at 60 °C. After stirring for 3 h at 60 °C, the mixture was evaporated and azeotropically evaporated with toluene (twice). The solid residue was chromatographed with a short column eluting with 30:1 $CHCl_3$–MeOH to give 6.58 g (94%) of **5**, pure enough for elemental analysis without further purification; mp 93–95.5 °C, $[\alpha]_D^{25}$ −122° (*c* 1.0, MeOH); ν_{max} broad 3400 (OH) and 1530 cm^{-1} (C=C–NO_2). Anal. Calcd for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 41.11; H, 5.53; N, 6.93.

*Methyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-*C*-nitro-β-*D*-*erythro*-hex-2-enopyranoside* (**6**). —A solution of **5** (700 mg, 3.41 mmol) in Ac_2O (7 mL) was cooled to −20 °C, and a

catalytic amount of $BF_3 \cdot Et_2O$ was added. After stirring for 6 min, MeOH (10 mL) was slowly added and the mixture was stirred for 30 min at 0 °C and evaporated. The residue was azeotropically evaporated with toluene and diluted with EtOAc. The organic layer was washed with aq satd NaCl (twice), dried, and evaporated to give light-yellow crystals of **6** in almost quantitative yield; mp 55.5–57 °C (*i*-PrOH), $[\alpha]_D^{25}$ −6° (*c* 1.2, CH_2Cl_2); ν_{max} 1750 (OAc) and 1535 cm^{-1} (C=C–NO_2). Anal. Calcd for $C_{11}H_{15}NO_8$: C, 45.68; H, 5.23; N, 4.84. Found: C, 45.80; H, 4.99; N, 4.77.

*Methyl 2,3-dideoxy-3-*C*-nitro-α-*D-threo-*hex-2-enopyranoside* (**9**).—A dispersion of **7** [21] (1.0 g, 3.41 mmol) in 90% aq AcOH (20 mL) was heated at 50 °C. After stirring for 6 h at 50 °C, the mixture was evaporated and azeotropically evaporated with toluene (twice). The solid residue was recrystallized from $CHCl_3$–toluene to give 0.22 g (31%) of **9**; mp 98–100 °C, $[\alpha]_D^{25}$ +41° (*c* 1.0, MeOH); ν_{max} broad 3410 (OH) and 1540 cm^{-1} (C=C–NO_2). Anal. Calcd for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 40.70; H, 5.60; N, 7.03.

*Methyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-*C*-nitro-α-*D-threo-*hex-2-enopyranoside* (**10**).—A solution of **9** (90 mg, 0.44 mmol) in Ac_2O (1 mL) was cooled to −10 °C, and a catalytic amount of $BF_3 \cdot Et_2O$ was added. After 1 h, EtOH (1 mL) was slowly added below 5 °C and the mixture was evaporated. The residue was azeotropically evaporated with toluene and diluted with EtOAc. The organic layer was washed with water (4 × 10 mL), dried, and evaporated to give 70 mg (55%) of **10** as a syrup, which was pure enough for elemental analysis; $[\alpha]_D^{25}$ −38° (*c* 1.1, CH_2Cl_2); ν_{max} 1750 (OAc) and 1540 cm^{-1} (C=C–NO_2). Anal. Calcd for $C_{11}H_{15}NO_8$: C, 45.68; H, 5.23; N, 4.84. Found: C, 45.80; H, 4.99; N, 4.77.

*Methyl 2,3-dideoxy-3-*C*-nitro-β-*D-threo-*hex-2-enopyranoside* (**11**).—A dispersion of **8** [22] (2.17 g, 7.40 mmol) in 90% aq AcOH (50 mL) was heated at 50 °C. After stirring for 4 h at 50 °C, the mixture was evaporated and azeotropically evaporated with toluene (twice). The resulting residue was chromatographed with 50:1 and 10:1 $CHCl_3$–MeOH to give 1.03 g (68%) of **11**; mp 65–68 °C, $[\alpha]_D^{25}$ −60° (*c* 0.9, MeOH); ν_{max} broad 3450 (OH) and 1535 cm^{-1} (C=C–NO_2). Anal. Calcd for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 40.98; H, 5.43; N, 6.80.

*Methyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-*C*-nitro-β-*D-threo-*hex-2-enopyranoside* (**12**).—A solution of **11** (50 mg, 0.24 mmol) in Ac_2O (1 mL) was cooled to −10 °C, and a catalytic amount of $BF_3 \cdot Et_2O$ was added. After 2 h, MeOH (5 mL) was slowly added below 5 °C and the mixture was evaporated below 40 °C. The residue was azeotropically evaporated with toluene and diluted with EtOAc. The organic layer was washed with water (4 × 20 mL), dried, and evaporated to give 40 mg (99%) of **12**, which was pure enough for elemental analysis; mp 75–77 °C, $[\alpha]_D^{25}$ −99° (*c* 1.0, MeOH); ν_{max} 1730 (OAc) and 1530 cm^{-1} (C=C–NO_2); ^1H NMR: NOE difference spectrum: H-1 (12%), H-4 (15%), and H-6′ (5%) irradiated at H-5 and H-2 (8%), H-5 (11%), and OMe (5%) irradiated at H-1. Anal. Calcd for $C_{11}H_{15}NO_8$: C, 45.68; H, 5.23; N, 4.84. Found: C, 45.80; H, 4.95; N, 4.77.

*Methyl 6-*O*-acetyl-2,3,4-trideoxy-3-*C*-nitro-α-*D-glycero-*hex-3-enopyranoside* (**13**).—(*a*) From **4**. To a mixture of **4** (100 mg, 0.35 mmol), $NaBH_4$ (20 mg, 0.52 mmol), toluene (5 mL), and H_2O (1.2 mL) was added 2 mg of the catalyst at 0 °C. After stirring for 2 h at 0 °C, the mixture was partitioned between M aq HCl (10 mL) and EtOAc (20

mL). The organic layer was washed with satd aq NaCl (twice), dried, and evaporated. The residue was chromatographed with 25:1 toluene–EtOAc to give 58 mg (73%) of **13**.

Similar treatment of **4** (100 mg, 0.35 mmol) with $NaBD_4$ (20 mg, 0.48 mmol) afforded 52 mg (65%) of **14**.

(*b*) From **25**. A stirred solution of **25** (20 mg, 0.08 mmol) and Et_3N (65 mg, 0.64 mmol) in CH_2Cl_2 (3 mL) was cooled to −20 °C, to which MsCl (35 mg, 0.31 mmol) was slowly added. After 5 h, the mixture was quenched by M aq HCl and diluted with CH_2Cl_2 (30 mL), washed with aq satd NaCl (twice), dried, and evaporated to a yellow syrup. The syrup was chromatographed with 100:1 and 50:1 toluene–EtOAc to give 18 mg (97%) of **13**, identical with an authentic sample by ^1H NMR spectroscopy.

Similar reaction of a monodeuterio derivative of **25**, in which the axial position at C-2 was deuterated, gave **14** in 95% yield.

(*c*) From **10**. A similar heterogeneous reaction of **10** (90 mg, 0.31 mmol) with $NaBD_4$ (15 mg, 0.36 mmol) afforded 40 mg (55%) of **14**.

Physical data for **13**: syrup, $[\alpha]_D^{25}$ +159° (*c* 1.2, CH_2Cl_2); ν_{max} 1740 (OAc) and 1520 cm^{-1} (C=C–NO_2). Anal. Calcd for $C_9H_{13}NO_6$: C, 46.75; H, 5.67; N, 6.06. Found: C, 46.70; H, 5.70; N, 5.89.

*Methyl 6-*O*-acetyl-2,3,4-trideoxy-3-*C*-nitro-β-*D*-glycero-hex-3-enopyranoside* (**15**).—(*a*) From **6**. To a mixture of **6** (496 mg, 1.71 mmol), $NaBH_4$ (100 mg, 2.64 mmol), toluene (20 mL), and H_2O (5 mL) was added 2 mg of the catalyst at 0 °C. After stirring for 2 h at 0 °C, the mixture was partitioned between M aq HCl (10 mL) and EtOAc (20 mL). The organic layer was washed with satd aq NaCl (twice), dried, and evaporated. The residue was chromatographed with 25:1 toluene–EtOAc to give 320 mg (81%) of **15**.

Similar treatment of **6** (50 mg, 0.17 mmol) with $NaBD_4$ (10 mg, 0.24 mmol) afforded 28 mg (70%) of **16**.

(*b*) From **27**. A stirred solution of **27** (20 mg, 0.08 mmol) and Et_3N (65 mg, 0.64 mmol) in CH_2Cl_2 (3 mL) was cooled to −20 °C, and MsCl (35 mg, 0.31 mmol) was slowly added. After 5 h, the mixture was quenched by M aq HCl and diluted with CH_2Cl_2 (30 mL), washed with aq satd NaCl (twice), dried, and evaporated to a yellow syrup. The syrup was chromatographed with 100:1 and 50:1 toluene–EtOAc to give 18 mg (97%) of **15**, identical with an authentic sample by ^1H NMR spectroscopy.

Similar reaction of a monodeuterio derivative of **27**, in which the equatorial position at C-2 was deuterated, gave **16** in 93% yield.

(*c*) From **12**. Similar heterogeneous reaction of **12** (50 mg, 0.17 mmol) with $NaBD_4$ (8 mg, 0.19 mmol) afforded 25 mg (63%) of **16**.

Physical data for **15**: syrup, $[\alpha]_D^{25}$ −83° (*c* 1.5, CH_2Cl_2); ν_{max} 1740 (OAc) and 1520 cm^{-1} (C=C–NO_2); ^1H NMR: NOE difference spectrum: H-5 (6%), OMe (7%), and H-2e (7%) irradiated at H-1, and H-1 (7%), H-4 (9%), H-6 (6%), and H-6′ (4%) irradiated at H-5. Anal. Calcd for $C_9H_{13}NO_6$: C, 46.75; H, 5.67; N, 6.06. Found: C, 46.69; H, 5.63; N, 6.01.

*Methyl 6-*O*-acetyl-2,4-dideoxy-α-*D*-glycero-hexopyranosid-3-ulose* (**20**).—A solution of **4** (200 mg, 0.69 mmol) in MeOH (5 mL) was cooled to −20 °C, and $NaBH_4$ (260 mg, 6.87 mmol) was added. After 10 min, the mixture was quenched by M aq HCl, diluted with CH_2Cl_2 (40 mL), washed with aq satd NaCl (twice), dried, and evaporated.

The syrup was chromatographed with 100:1 and 25:1 toluene–EtOAc to give 109 mg (78%) of **20** as a syrup; $[\alpha]_D^{25}$ +122° (*c* 1.1, CH_2Cl_2); ν_{max} 1740 (OAc) and 1720 (shoulder C=O) cm^{-1}. Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.20; H, 7.16.

*Methyl 6-O-acetyl-2,4-dideoxy-β-*d-glycero-*hexopyranosid-3-ulose* (**21**).—A solution of **6** (30 mg, 0.10 mmol) in MeOH (3 mL) was cooled to −20 °C, and $NaBH_4$ (40 mg, 1.06 mmol) was added. After 10 min, the mixture was partitioned between M aq HCl and CH_2Cl_2 (40 mL). The organic layer was washed with aq satd NaCl (two times), dried, and evaporated to give a syrup, which was chromatographed with 50:1 toluene–EtOAc to give 15 mg (72%) of **21** as a syrup; $[\alpha]_D^{25}$ −89° (*c* 0.52, CH_2Cl_2); ν_{max} broad 1740 cm^{-1} (OAc) and (C=O). Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.20; H, 7.03.

*Methyl 2,3-dideoxy-3-*C*-nitro-α-*D-arabino-*hexopyranoside* (**24**).—A stirred solution of **22** [12,13] (400 mg, 1.35 mmol) in 70% aq AcOH (40 mL) was warmed at 60 °C. After 4 h, the mixture was evaporated and subjected to repeated evaporation with toluene (twice). The residue was chromatographed with 9:1 $CHCl_3$–MeOH to give 240 mg (86%) of **24**; mp 73–75.5 °C, $[\alpha]_D^{25}$ +133° (*c* 0.5, CH_2Cl_2); ν_{max} (Nujol) 3250 and 3200 (OH), 1560 and 1545 cm^{-1} (NO_2). Anal. Calcd for $C_7H_{13}NO_6$: C, 40.58; H, 6.32; N, 6.76. Found: C, 40.42; H, 6.41; N, 6.81.

Similar debenzylidenation of a derivative of **22**, in which the axial position at C-2 was deuterated [14], gave the corresponding monodeuterio derivative of **24**.

*Methyl 6-O-acetyl-2,3-dideoxy-3-*C*-nitro-α-*D-arabino-*hexopyranoside* (**25**).—A stirred solution of **24** (130 mg, 0.63 mmol) and pyridine (2 mL) was cooled to −10 °C, and AcCl (64 mg, 0.82 mmol) was slowly added. After 4 h at −10 °C, MeOH was added to the mixture at such a rate that the temperature did not rise over 5 °C. After stirring for 1 h, the mixture was diluted with EtOAc (30 mL), washed with M aq HCl, aq satd NaCl (twice), dried, and evaporated. The syrup was chromatographed with 20:1 toluene–EtOAc to give 110 mg (70%) of **25** as a syrup, which was pure enough for elemental analysis; $[\alpha]_D^{25}$ +69° (*c* 1.2, CH_2Cl_2); ν_{max} broad 3450 (OH), 1740 (OAc), and 1550 cm^{-1} (NO_2). Anal. Calcd for $C_9H_{15}NO_7$: C, 43.38; H, 6.07; N, 5.62. Found: C, 43.56; H, 5.78; N, 6.01.

Similar acetylation of the monodeuterio derivative of **24** gave the axially deuterated derivative of **25**.

*Methyl 2,3-dideoxy-3-*C*-nitro-β-*D-arabino-*hexopyranoside* (**26**).—A stirred solution of **23** [12] (560 mg, 1.90 mmol) in 90% aq AcOH (50 mL) was warmed at 60 °C. After 3 h, the mixture was evaporated and subjected to repeated evaporation with toluene (twice). The residue was chromatographed with 100:1 and 30:1 $CHCl_3$–MeOH to give 260 mg (66%) of **26**; mp 75.5–77 °C, $[\alpha]_D^{25}$ −44° (*c* 0.3, $CHCl_3$); ν_{max} 3400 and 3300 (OH) and 1550 cm^{-1} (NO_2). Anal. Calcd for $C_7H_{13}NO_6$: C, 40.58; H, 6.32; N, 6.76. Found: C, 40.32; H, 6.21; N, 6.81.

Similar debenzylidenation of the monodeuterio derivative of **23**, whose equatorial position at C-2 was deuterated [14], gave the equatorially deuterated derivative of **26**.

*Methyl 6-O-acetyl-2,3-dideoxy-3-*C*-nitro-β-*D-arabino-*hexopyranoside* (**27**).—A stirred solution of **26** (50 mg, 0.24 mmol) and pyridine (2 mL) was cooled to −20 °C, and AcCl (33 mg, 0.42 mmol) was slowly added. The mixture was kept for 5 h at 0 °C,

and then cooled to −20 °C. To the solution was added MeOH (1 mL) and it was diluted with CH_2Cl_2 (30 mL), washed with M aq HCl, aq satd NaCl (twice), dried, and evaporated. The syrup was chromatographed with 30:1 and 10:1 toluene–EtOAc to give 53 mg (88%) of **27**, which was pure enough for elemental analysis; mp 48–50 °C, $[\alpha]_D^{25}$ −84° (*c* 1.0, CH_2Cl_2); ν_{max} broad 3420 (OH), 1720 (OAc), and 1550 cm^{-1} (NO_2). Anal. Calcd for $C_9H_{15}NO_7$: C, 43.38; H, 6.07; N, 5.62. Found: C, 43.61; H, 6.00; N, 5.55.

Similar acetylation of the monodeuterio derivative of **26** gave the equatorially deuterated derivative of **27**.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-α-*D*-lyxo-hexopyranoside* (**28**).—A mixture of **7** (30 mg, 0.10 mmol), $NaBH_4$ (10 mg, 0.26 mmol), a catalytic amount of the catalyst, toluene (5 mL), and H_2O (2 mL) was stirred for 3 h at room temperature and then partitioned between M aq HCl and CH_2Cl_2. The organic layer and extracts were washed with aq satd NaCl (twice), dried, and evaporated. The residue was chromatographed with 100:1 and 30:1 toluene–EtOAc to give 29 mg (95%) of **28**; mp 102–104 °C, $[\alpha]_D^{25}$ +144° (*c* 1.1, $CHCl_3$); ν_{max} 1550 cm^{-1} (NO_2). Anal. Calcd for $C_{14}H_{17}NO_6$: C, 56.95; H, 5.80; N, 4.74. Found: C, 57.08; H, 5.50; N, 4.73.

Similar reduction of **7** (10 mg, 0.03 mmol) with $NaBD_4$ (3 mg, 0.07 mmol) in toluene (5 mL) and H_2O (2 mL) in the presence of a catalytic amount of the catalyst gave a 5:1 mixture (10 mg, 99%) of axially and equatorially monodeuterated derivatives of **28**.

*Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-β-*D*-lyxo-hexopyranoside* (**29**).—A mixture of **8** (20 mg, 0.07 mmol), $NaBH_4$ (10 mg, 0.26 mmol), a catalytic amount of the catalyst, toluene (5 mL), and H_2O (2 mL) was stirred for 3 h at room temperature and then partitioned between M aq HCl and CH_2Cl_2. The organic layer and extracts were washed with aq NaCl (twice), dried, and evaporated. The residue was chromatographed with 100:1 and 30:1 toluene–EtOAc to give 19 mg (94%) of **29**; mp 165–167 °C, $[\alpha]_D^{25}$ +15° (*c* 0.3, $CHCl_3$); ν_{max} 1545 cm^{-1} (NO_2). Anal. Calcd for $C_{14}H_{17}NO_6$: C, 56.95; H, 5.80; N, 4.74. Found: C, 57.23; H, 5.55; N, 4.99.

Similar reduction of **8** (20 mg, 0.07 mmol) with $NaBD_4$ (7 mg, 0.17 mmol) in toluene (5 mL) and H_2O (2 mL) in the presence of a catalytic amount of the catalyst for 3 h gave a 1:1.7 mixture (15 mg, 74%) of axially and equatorially deuterated derivatives of **29**.

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