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Preparation of 2-*C*- and 3-*C*-cyano-2-enopyranoside derivatives and their epoxidation

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Abstract—Methyl 4,6-*O*-benzylidene-2-*C*- and 3-*C*-cyano-2,3-dideoxy-D-*erythro*-hex-2-enopyranosides and -2-enitols were prepared and their epoxidation was performed.

Keywords: Cyanosugar; Epoxidation; Stereochemistry; Nucleophilic addition reaction

1. Introduction

Nucleophilic addition reactions of a carbon–carbon double bond activated by an electron-withdrawing group is one of the most fundamental reactions in organic chemistry. It is used in a wide range of organic syntheses.[1]

The stereochemistry of these reactions has been subjected to considerable research over the past years.[2] In a six-membered substrate one of the authors proposed that an approaching direction of a nucleophile seems to be controlled by the following three factors.[3] (1) Factor 1: The nucleophile comes from the opposite side of substituent(s), especially at the γ-position of an activated carbon–carbon double bond, due to steric and electrostatic repulsion. (2) Factor 2: It approaches from the axial side to lead a chair-like intermediate due to stereoelectronic control;[4] otherwise a boat like intermediate is formed. (3) Factor 3: It attacks from the same side of a substituent at the β′-position (*syn* addition) if an intermediate anion suffers from steric ($A^{(1,3)}$ strain[5]) and electrostatic repulsion (Fig. 1). Factor 3 should be important in the case of α-nitro alkenes. Different from a nitro group, a linear cyano group gives no $A^{(1,3)}$ strain in an anionic intermediate; therefore, Factor 3 plays a relatively unimportant role in the case of cyano alkenes.[†] To confirm this speculation we prepared 2-*C*-cyano-2-enopyranosides **3** and **4**, 3-*C*-cyano-2-enopyranosides **14** and **15**, and 3-*C*-cyano-2-enitol **16** and performed their epoxidation.

The epoxidation of methyl 3-nitro-β-D-2-enopyranoside and its α-anomer exclusively afforded the allo and mannopyranoside, respectively, in high yields.[6] However, in methyl 2-nitro-α-D-2-enopyranoside, the direction of approach strongly depended on the peroxides used. Hydrogen peroxide afforded the *allo* isomer, whereas *tert*-butyl hydroperoxide gave the *manno* isomer.[7] Therefore, we used these two peroxides herewith.

Furthermore, epoxidation of methyl 2-*C*-nitro-β-D-2-enopyranoside (**36**) and 1,5-anhydro-3-*C*-nitro-hex-2-enitol (**38**) have been performed for comparison with those of the corresponding cyano alkenes.

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† Electrostatic repulsion still remains, because distance between the anionic nitrogen atom of cyano group and the substituent at the β′-position is longer in the case of *syn* addition than that of *anti* addition.

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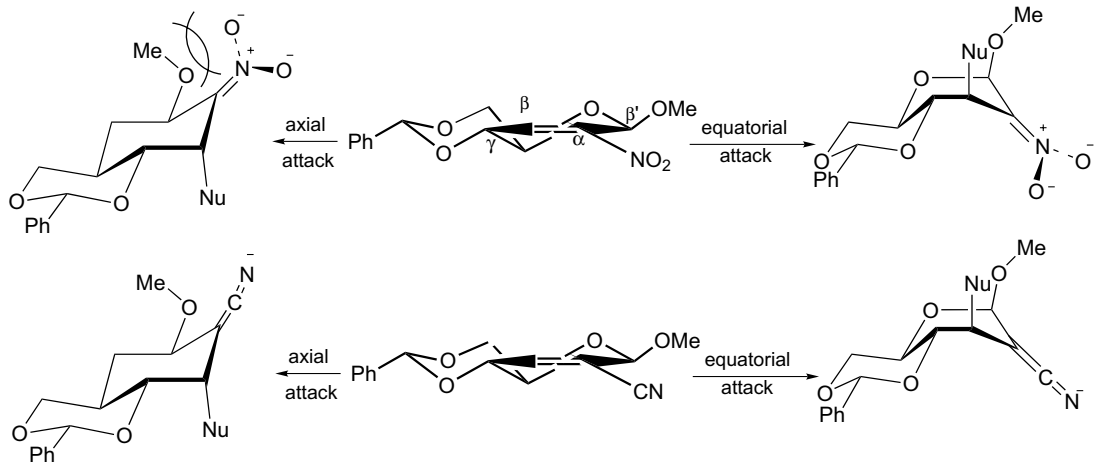


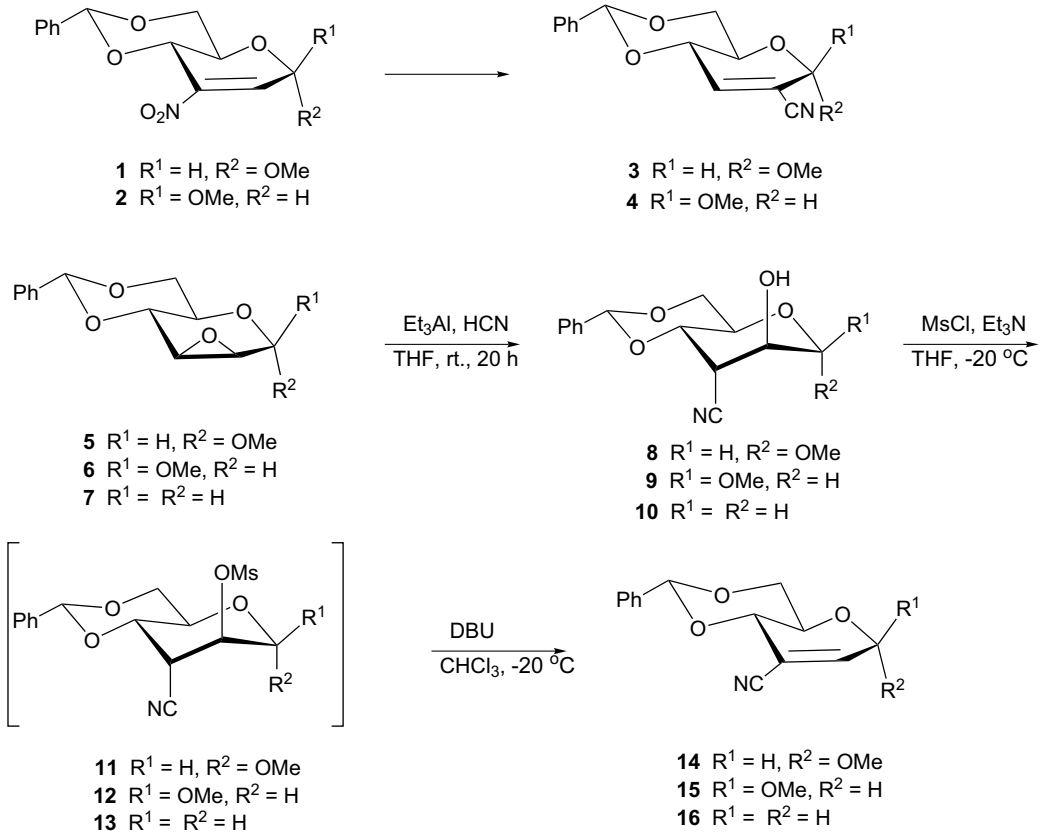
Figure 1.

2. Results and discussion

2.1. Preparation of α-cyano olefins

Methyl 2-*C*-cyano-α- **3**[8] and -β-D-2-enopyranosides **4**[9] were prepared from the corresponding 3-*C*-nitro-2-enopyranosides **1** and **2**, respectively, by the previously reported method with slight modification (Scheme 1).

Methyl 3-*C*-cyano-α-D-2-enopyranoside **14** was synthesized through diaxial opening of epoxide **5** with hydrogen cyanide in the presence of either triethyl aluminum,[10] cyanotrimethylsilane using aluminum chloride as a catalyst,[11] or diethyl aluminum cyanide.[12] Epoxide **5** was opened with triethyl aluminum and hydrogen cyanide, followed by the epimerization of the cyano group, mesylation of the hydroxyl group, and elimination of



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

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

5 R^1 = H, R^2 = OMe
6 R^1 = OMe, R^2 = H
7 R^1 = R^2 = H

8 R^1 = H, R^2 = OMe
9 R^1 = OMe, R^2 = H
10 R^1 = R^2 = H

11 R^1 = H, R^2 = OMe
12 R^1 = OMe, R^2 = H
13 R^1 = R^2 = H

14 R^1 = H, R^2 = OMe
15 R^1 = OMe, R^2 = H
16 R^1 = R^2 = H

Scheme 1.

methanesulfonic acid. When the epimerization was omitted, the yield was improved.

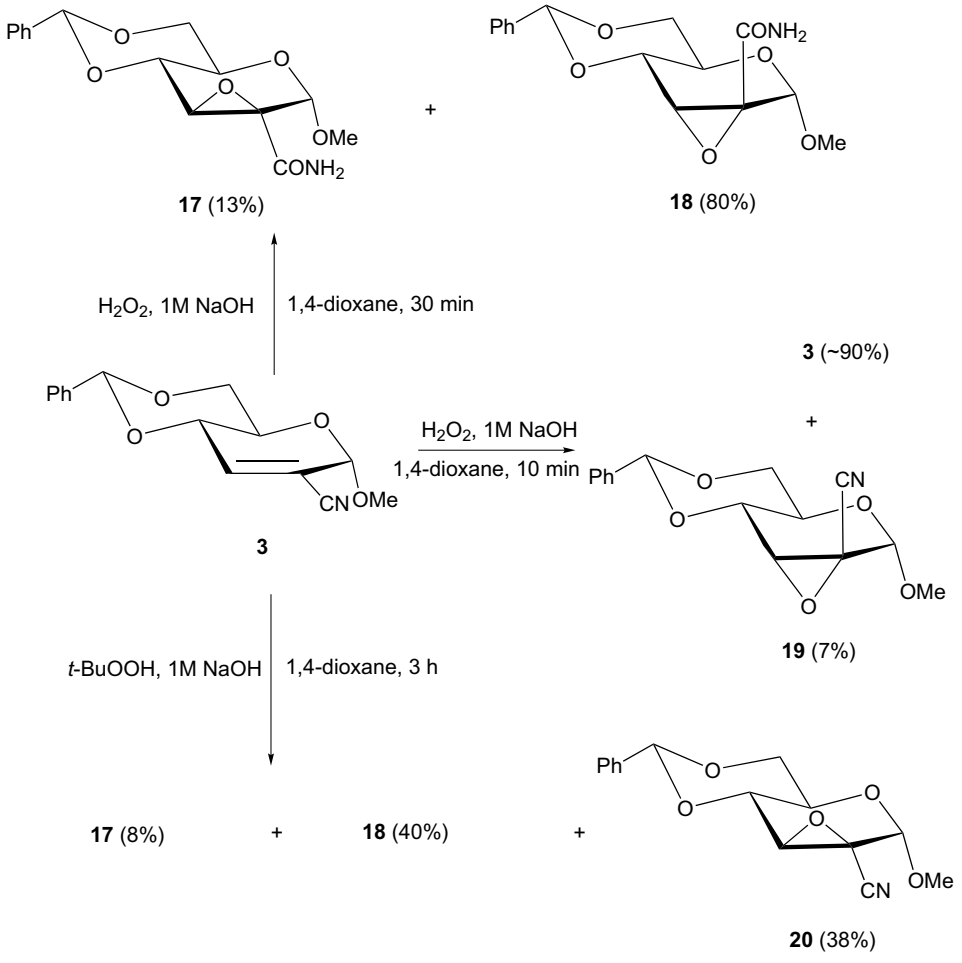
Similar reaction of 2,3-anhydro-β-D-mannopyranoside **6** and 1,5:2,3-dianhydro-D-mannitol **7** afforded 3-*C*-cyano-β-D-2-enopyranoside **15** and 1,5-anhydro-3-*C*-cyano-2-enitol **16**, respectively (Scheme 1).

2.2. Epoxidation

Thus prepared cyano alkenes **3**, **4**, and **14**–**16** were each separately treated with hydrogen peroxide and bulky *tert*-butyl hydroperoxide in the presence of aqueous M sodium hydroxide.

Treatment of 2-*C*-cyano-α-D-2-enopyranosides **3** with 30% aqueous hydrogen peroxide for 30 min afforded a 1:6 mixture of *manno* **17** and *allo* epoxides **18** having a carbamoyl group. Under the conditions employed, the cyano group was hydrated to the carbamoyl group. From the steric aspect it is very important whether the hydration of the cyano group occurred after or before the epoxidation, because the carbamoyl group is not linear and suffers from $A^{(1,3)}$ strain in the anionic intermediate. When the reaction was performed under mild conditions, unreacted **3** was recovered in 90% yield, along with 2-*C*-cyano-allopyranoside **19** in 7% yield, suggesting that the cyano group converted into the carbamoyl group after epoxidation. In fact cyano epoxide **19** was changed to carbamoyl epoxide **18** under the conditions employed for preparation of **17** and **18**. Epoxidation with 70% *tert*-butyl hydroperoxide afforded 2,3-anhydro-2-*C*-cyano-mannopyranoside **20**, the carbamoyl derivatives having *manno* **17**, and *allo* configuration **18** in 38, 8, and 40% yields, respectively (Scheme 2).

Epoxidation of β-D-anomer **4** with hydrogen peroxide for 30 min provided a 1:2 mixture of the carbamoyl derivatives having *manno* configuration **21** and *allo* configuration **22** in 89% yield. When the reaction time was reduced to 5 min, a complicated mixture was obtained from which a small amount of hydroperoxide **23** having the *gluco* configuration was isolated. Hydroperoxide **23** was converted into carbamoyl epoxide **21** by treatment with *tert*-butyl hydroperoxide in the presence of M sodium hydroxide. Similar epoxidation of **4** with *tert*-butyl hydroperoxide for 6.5 h afforded *manno* epoxide **21** in high yield. A complicated mixture was obtained when the reaction was stopped at 5 min. Besides



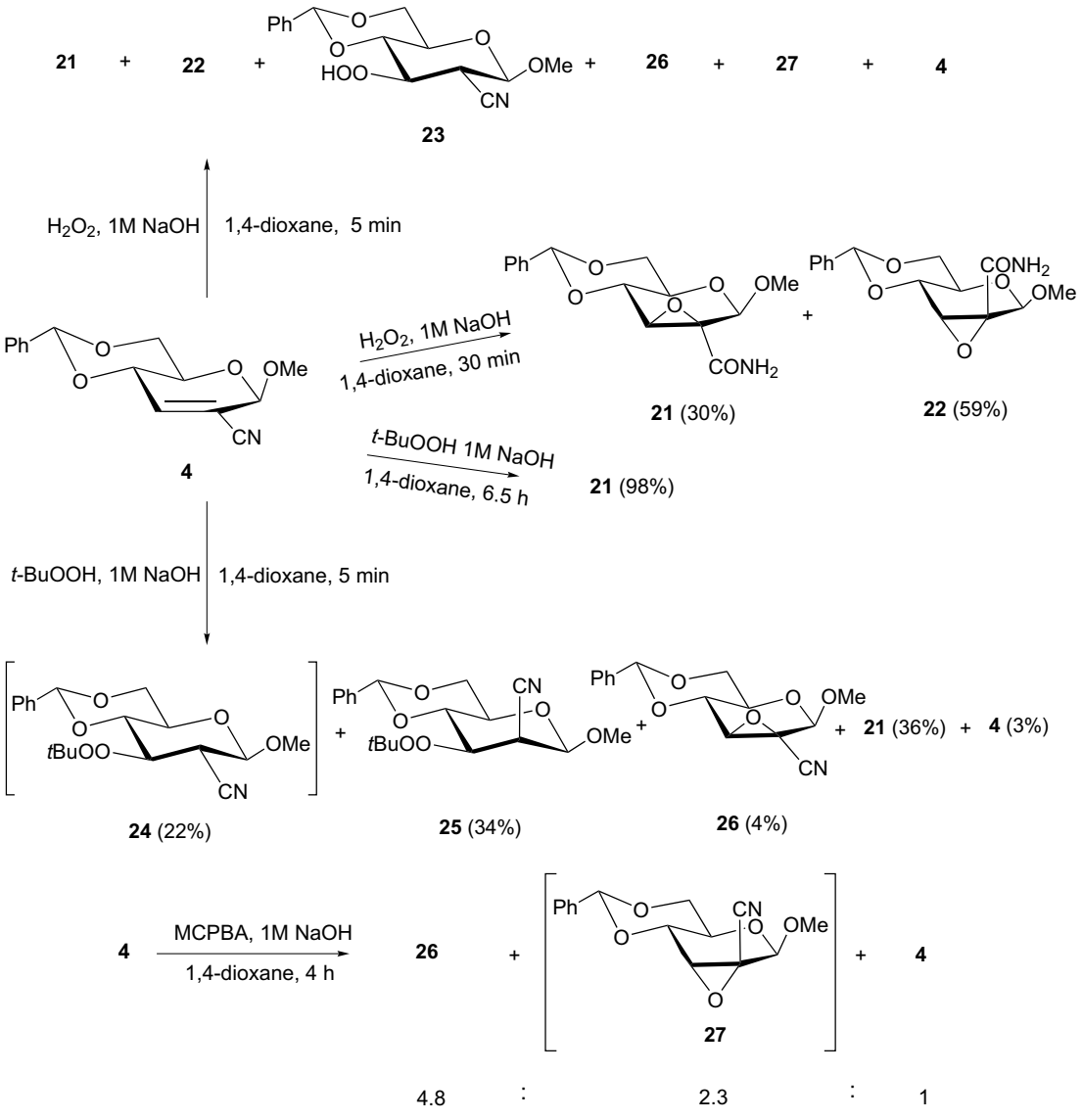
Scheme 2.

carbamoyl derivative **21**, peroxides **24** and **25** were detected, from which peroxide **25** having the *manno* configuration was isolated, but its 2-epimer **24** was not. Treatment of peroxide **25** with *tert*-butyl hydroperoxide for 6.5 h gave carbamoyl epoxide **21** in high yield. Cyano epoxide **26**, together with its *allo* isomer **27**, became the major product from the treatment of **4** with *m*-chloroperoxybenzoic acid in the presence of M sodium hydroxide. Although cyano epoxide **27** was not isolated, its 2-epimer **26** was isolated (Scheme 3).

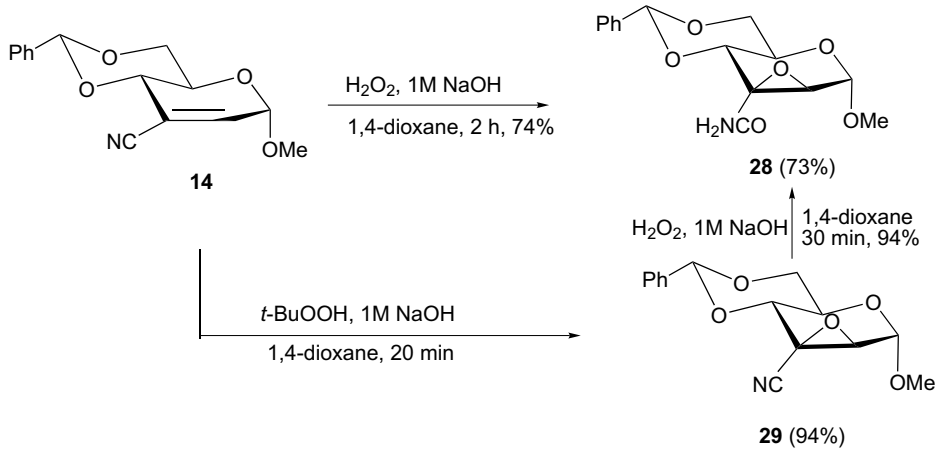
Reaction of 3-*C*-cyano-α-D-2-enopyranoside **14** with hydrogen peroxide afforded 2,3-anhydro-3-*C*-carbamoyl-α-D-mannopyranoside **28** in 74% yield. When compound **14** was treated with *tert*-butylperoxide, 2,3-anhydro-3-*C*-cyano-α-D-mannopyranoside **29** was formed in 94% yield. Epoxide **29** was converted into carbamoyl derivative **28** by treatment with hydrogen peroxide in the presence of M sodium hydroxide (Scheme 4).

Treatment of 3-*C*-cyano-β-D-2-enopyranoside **15** with hydrogen peroxide for 1 h afforded the carbamoyl derivative **30** having the β-D-*allo* structure in almost quantitative yield. When the reaction was stopped at 3 min, 3-cyano-2-hydroperoxy-β-D-glucopyranoside **31** (20%) was isolated besides the starting material **15** (62%) and the carbamoyl derivative **30** (18%). Compound **30** was also obtained in 89% yield by treatment of **15** with *tert*-butyl hydroperoxide for 40 min (Scheme 5).

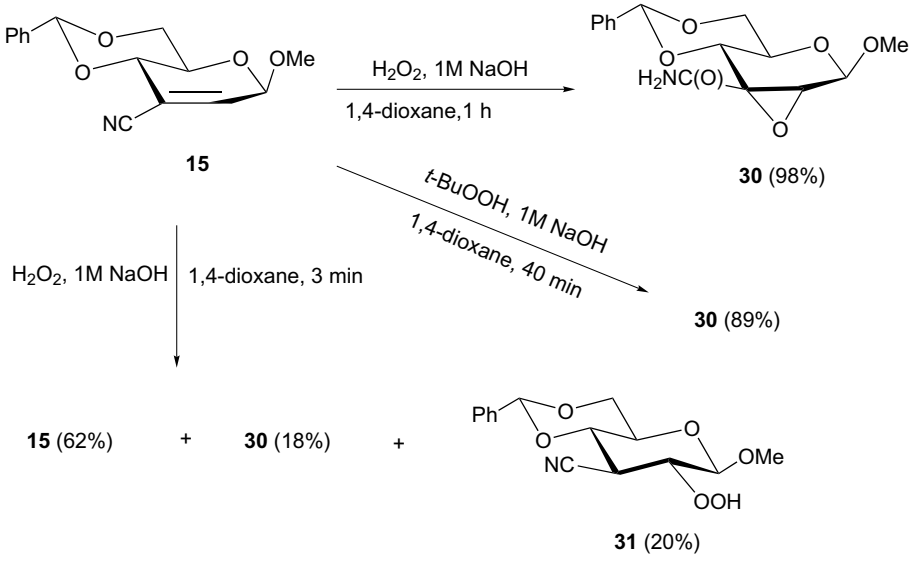
Similar treatment of 1,5-anhydro-3-*C*-cyano-2-enitol **16** with hydrogen peroxide for 1 h at room temperature caused double-bond migration instead of epoxidation, giving glucal **32** (30%) and allal **33** (60% yield). When the reaction temperature was lowered to 0 °C, the epox-



Scheme 3.



Scheme 4.



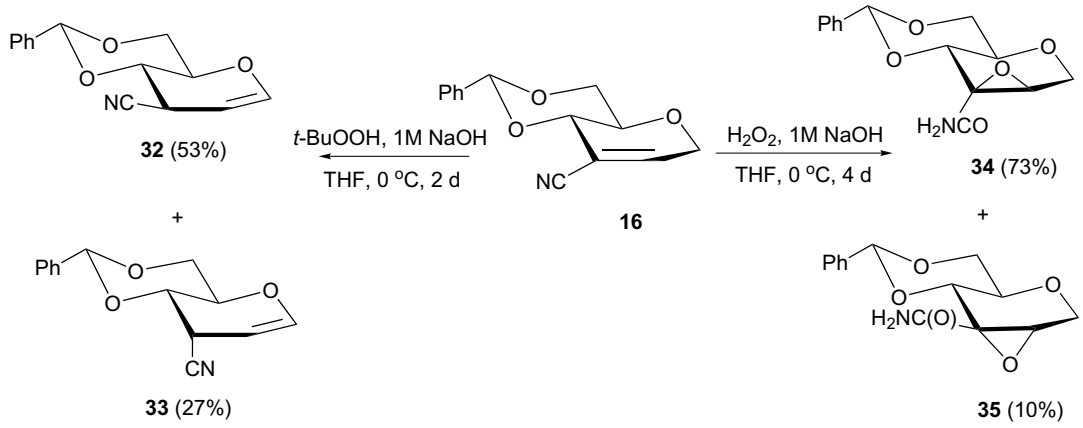
Scheme 5.

idation smoothly proceeded to yield amides **34** and **35** having the *manno* and *allo* configurations in 73% and 10% yields, respectively. However, the double-bond migration exclusively occurred by treatment of **16** with *tert*-butyl hydroperoxide even at 0 °C (Scheme 6).

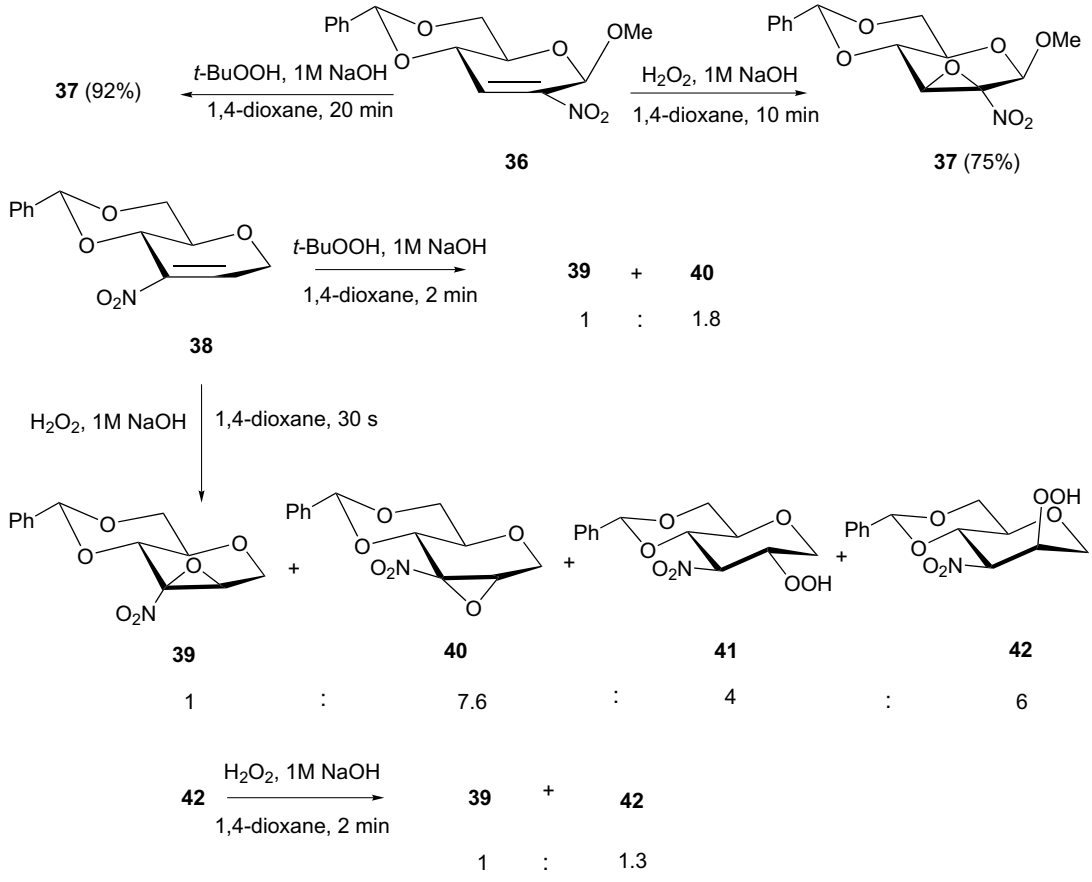
For comparison with these results, epoxidations of methyl 2-*C*-nitro-β-D-2-enopyranoside **36** and 1,5-anhydro-3-*C*-nitro-D-2-enitol **38** were performed. Treatment of **36** with hydrogen peroxide or *tert*-butyl hydroperoxide exclusively gave epoxide **37** having the *manno* configuration. Epoxidation of **38** became slightly complicated, because the hydroperoxide was detected at short reaction time, and epoxide **40** was almost completely decomposed on silica gel column chromatography. When the reaction was performed at room temperature and immediately stopped (30 s), epoxides **39** and **40** with the *manno* and *allo* configurations as well as hydroperoxides **41** and **42** having the *gluco* and *manno* configurations were formed in a ratio of 1:7.6:4:6. This ratio changed to 1:2.3:0.8:1 after 5 min. When hydroperoxide **42** having the *manno* configuration was similarly treated for 2 min, a 1:1.3 mixture of epoxide **39** and the starting peroxide **42** was obtained, but alternative epoxide **40** and 3-epimer **41** were not detected, indicating that the peroxidation is irreversible, that is, the present reaction was kinetically controlled (Scheme 7).

2.3. Configurational determination of the epoxides

The axial and equatorial anomeric protons of 1,5:2,3-dianhydro sugars as well as the anomeric proton (a singlet) and the benzylidene methine proton (a singlet) of 2-substituted 2,3-anhydro sugars isolated were also assigned by a NOESY spectrum. All chemical shifts



Scheme 6.



Scheme 7.

described herewith were recorded in chloroform-*d* with tetramethylsilane as an internal standard (Tables 1–3). Large coupling constants, $J_{4,5}$ 8.9–9.6 Hz, suggested that all of the 2,3-anhydro sugars thus prepared expectedly adopt the $^{0}H_{5}$ conformation.[13] The configurations of the epoxides thus prepared were determined as follows. In the 2,3-anhydro compounds the dihedral angle of trans relationship of hydrogen atoms between H-1 and H-2 or H-3 and H-4 is almost 90°; therefore, the coupling constant is close to 0 Hz.[6,13,14] This rule could be applied to 1,5-anhydro- and methyl 2,3-anhydrohexopyranosides except 2,3-anhydro-3-*C*-carbamoyl-β-D-allopyanosides **22**, in which the $J_{3,4}$ value was 0 Hz. Instead of the coupling constants, therefore, the chemical shift of H-1 (δ 5.62 for **21** and δ 5.05 for **22**) was used for assignment of the *manno* and *allo* configurations for

Table 1. ^{1}H NMR (400 MHz, $CDCl_3$) chemical shift (δ in ppm) of 2,3-anhydrohexopyranosides

	17	**18**	**19**[a]	**20**	**21**	**22**	**26**	**27**	**28**	**29**[a]	**30**	**37**
H-1	5.05(s)	5.60(s)	4.58(s)	4.97(s)	5.62(s)	5.05(s)	5.10(br s)	4.96(s)	4.93(s)	4.18(s)	4.88(s)	5.90(s)
H-2	—	—	—	—	—	—	—	—	3.44(s)	3.03(s)	3.43(s)	—
H-3	3.56(s)	3.62(br s)[b]	3.15(br s)	3.90(br s)	3.61(s)	3.76(s)	3.92(s)	3.96(d)	—	—	—	3.98(s)
H-4	3.77(d)	3.98(dd)	3.06(dd)	3.65(d)	3.75(d)	4.37(d)	3.71(d)	4.17(dd)	3.97(d)	3.27(d)	4.72(d)	3.76(d)
H-5	3.85(td)	4.04(td)	3.91(br dt)	3.82(td)	3.49(m)	4.00(ddd)	3.44(ddd)	3.43(dt)	3.88(td)	3.50(td)	3.64(ddd)	3.59(ddd)
H-6a	3.77(t)	3.72(t)	3.20(t)	3.72(t)	3.80(t)	3.71(t)	3.80(t)	3.80(t)	3.75(t)	3.19(t)	3.80(t)	3.82(t)
H-6e	4.28(dd)	4.28(dd)	3.84(dd)	4.27(dd)	4.32(dd)	4.28(dd)	4.32(dd)	4.29(dd)	4.32(dd)	3.84(dd)	4.29(dd)	4.35(dd)
PhCH	5.58(s)	5.56(s)	5.14(s)	5.55(s)	5.55(s)	5.57(s)	5.56(s)	5.56(s)	5.60(s)	5.08(s)	5.66(s)	5.56(s)
OMe	3.56(s)	3.48(s)	2.92(s)	3.56(s)	3.61(s)	3.57(s)	3.60(s)	3.66(s)	3.48(s)	2.81(s)	3.52(s)	3.66(s)

[a] In C_6D_6, data in $CDCl_3$ see Section 3.
[b] br—broad.

Table 2. ^{1}H NMR (400 MHz, in $CDCl_3$) chemical shift (δ in ppm) of 1,5:2,3-dianhydrohexitols

	34	**35**	**39**	**40**
H-1a	4.02(dd)	4.02(br d)	4.09(dd)	3.99(d)
H-1e	4.26(d)	4.14(dd)	4.22(d)	4.23(dd)
H-2	3.50(br s)[a]	3.52(d)	3.85(br s)	3.91(d)
H-3	—	—	—	—
H-4	3.95(d)	4.67(d)	4.04(d)	5.01(d)
H-5	3.33(td)	3.63(ddd)	3.47(td)	3.59(td)
H-6a	3.72(t)	3.83(t)	3.76(t)	3.80(t)
H-6e	4.33(dd)	4.25(dd)	4.35(dd)	4.30(dd)
PhCH	5.60(s)	5.56(s)	5.61(s)	5.72(s)

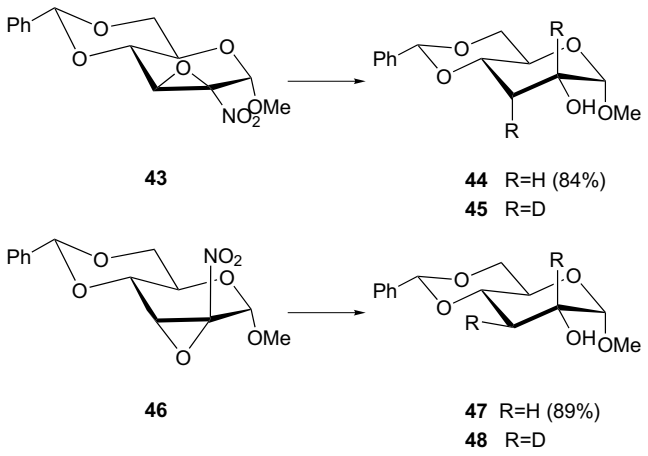
[a] br—broad.

21 and **22**, respectively. The hydrogen atom occupied the same side of a carbamoyl group appears in a lower field than that occupied the opposite side because of the anisotropy of the carbamoyl group. In fact, for example, the anomeric proton of 2-carbamoyl-α-D-mannopyranoside **17** (δ 5.05; $J_{3,4}$ 0 Hz) appeared in a higher field than that of 2-carbamoyl-α-D-allopyranoside **18** (δ 5.60; $J_{3,4}$ 0.8 Hz). The *manno* configuration for **21** was confirmed by transformation of 3-hydroperoxy-β-D-glucopyranoside **23** into **21**. The configuration of 1,5:2,3-dianhydro-3-*C*-carbamoyl derivatives **34** and **35** could be assigned by the coupling constant ($J_{1a,2}$ 1.0 and $J_{1e,2}$ 0 Hz for **34**, and $J_{1a,2}$ 0 and $J_{1e,2}$ 3.5 Hz for **35**) and chemical shift of H-4 (δ 3.95 for **34** and δ 4.67 for **35**). Methyl 3-cyano-α- **14** and -β-2-enopyranoside **15** gave only one isomer, that is, *manno* isomer **28** from **14** and *allo* isomer **30** from **15**. Not only the coupling constants ($J_{1,2}$ 0 Hz), but also chemical shift of H-4 close to the corresponding 1,5-anhydro sugar supports the respective configuration; δ 3.97 for **28** versus δ 3.95 for **34** and δ 4.72 for **30** versus δ 4.67 for **35**. For cyano epoxides $J_{3,4}$ values and H-1 chemical shifts of the *allo* isomer **19** is 1.2 Hz and δ 5.07, whereas that of *manno* isomer **20** is 0 Hz and δ 4.97. Both compounds **19** and **20** were hydrated to the carbamoyl derivatives **18** and **17**, respectively. Although isolation of 2-*C*-cyano epoxide **27** having the *allo* configuration is not accomplished, its configuration was determined by comparison of ^{1}H NMR data with those of the alternative isomer **26**; δ 4.96 (H-1) and $J_{3,4}$ 1.2 Hz for **27** and δ 5.10 (H-1) and $J_{3,4}$ 0 Hz for **26**. Both cases, **19** versus **20** and **26** versus **27**, the hydrogen atom occupied the same side of cyano group again appeared slightly lower field than that of alternative one. 3-*C*-Cyano epoxide **29** having $J_{1,2}$ 0 Hz was hydrolyzed to the carbamoyl derivative **28**. The difference of chemical shift was again observed in nitro epoxides. The configuration of 1,5:2,3-dianhydro-3-*C*-nitro derivatives **39** and **40** was determined by the coupling constant and chemical shift of H-4 ($J_{1a,2}$ 1.1, $J_{1e,2}$ 0 Hz, δ 4.04 for **39** and $J_{1a,2}$ 0, $J_{1e,2}$ 3.5 Hz, δ 5.01 for **40**) and confirmed by chemical transformation of hydroperoxide **42** having the *manno* structure into epoxide **39**. In the previous paper a satisfactory ^{1}H NMR spectrum of methyl 2,3-anhydro-2-*C*-nitro-α-D-allopyranoside (**46**) was not obtained because of its low solubil-

Table 3. Coupling constants (Hz) of 2,3-anhydro sugars (400 MHz, $CDCl_3$)

	17	**18**	**19**	**20**	**21**	**22**	**26**	**27**[a]	**28**	**29**	**30**	**34**	**35**	**37**	**39**	**40**
$J_{1a,1e}$	—	—	—	—	—	—	—	—	—	—	—	13.8	13.9	—	14.3	14.0
$J_{1a,2}$	—	—	—	—	—	—	—	—	—	—	0	1.0	0	—	1.1	0
$J_{1e,2}$	—	—	—	—	—	—	—	—	0	0	—	0	3.5	—	0	3.5
$J_{2,3}$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$J_{3,4}$	0	0.8	1.2	0	0	0	0	1.2	—	—	—	—	—	0	—	—
$J_{4,5}$	9.4	9.2	8.9	9.5	9.4	9.4	9.6	7.6	9.6	9.5	9.3	9.5	9.0	9.4	9.4	9.0
$J_{5,6a}$	10.0	10.2	10.1	10.3	10.3	10.4	9.8	10.3	10.3	10.2	10.3	9.7	8.9	10.4	10.7	10.4
$J_{5,6e}$	4.0	4.9	5.1	4.5	4.7	4.7	4.6	4.7	4.0	4.6	4.9	4.8	4.8	4.6	4.7	4.9
$J_{6a,6e}$	10.0	10.2	10.1	10.3	10.3	10.4	10.5	10.6	10.3	10.3	10.3	10.5	10.2	10.6	10.2	10.4

[a] $J_{1,4}$ 1.2 Hz.



Scheme 8.

ity in $CDCl_3$ and decomposition in hot DMSO-d_6;[7] however, an acceptable spectrum was recorded at 400 MHz in acetone-d_6, which revealed a $J_{3,4}$ value of 1.2 Hz. The chemical shift of H-1 again supported the assignment (δ 5.46 for **43** and δ 6.03 for **46**). Adequacy of the assignment was proved by reduction of **43** and its *manno* isomer **46** with lithium aluminum deuteride, in which a deuteride ion attacked from the opposite side of the epoxide ring[15] to give 3-deoxy-2,3-deuterio-α-D-allo **45** and -α–D-glucopyranoside **48**, respectively (Scheme 8). The *manno* structure for nitro epoxide **37**, the only product generated from methyl 2-*C*-nitro-β-2-enopyranoside **36**, was assigned on the basis of $J_{3,4}$ 0 Hz. It is noteworthy that H-1 chemical shift (δ 5.90) of **37** is close to that of **46** (δ 5.98) rather than that of **43** (δ 5.32).

2.4. Stereoselectivity of epoxidation

We discuss the stereochemistry assuming that a stereoelectronic effect inevitably operates. The anomeric effect[4] (Factor 4) is in operation in addition to the three factors mentioned in Section 1. Furthermore, Factor 3 plays an unimportant role in the case of linear cyano alkene, and the influence of Factor 1 increases with increasing bulkiness of nucleophile. Both hydrogen peroxide and *tert*-butyl hydroperoxide approached from the opposite side of anomeric methoxyl group of 3-*C*-cyano-2-enopyranosides **14** and **15**. The highly stereoselective axial attack to 3-*C*-cyano-α-D-enopyranoside **14** should be caused by the Factors 1, 2, and 4. In the case of β-anomer **15**, equatorial attack is favored by Factors 1 and 4, but disfavored by Factor 2. Equatorial attack exclusively occurred, suggesting that besides the Factors 1 and 4, synergetic electrostatic repulsion due to O-1 and O-5 prevents axial attack. In the case of 2-*C*-cyano-α-D-2-enopyranoside **3**, axial attack is favored by Factors 2 and 4, and equatorial attack is supported by Factor 1. Less bulky hydrogen peroxide predominantly added from the axial side; however, the more bulky *tert*-butyl hydroperoxide approached from both sides in almost equal ratio. In spite of the presence of unfavorable Factor 3, *tert*-butyl hydroperoxide almost exclusively added from the equatorial side of the α-anomer of nitro alkene **36** as had been mentioned in Section 1.[7] Therefore, we expected that *tert*-butyl hydroperoxide should exclusively attack from the equatorial side of cyanoalkene **3**, because Factor 3 is unimportant in the case of cyano alkene, but this is not the case. This unexpected result is probably explained by additional steric hindrance due to the deviation of the nitro group from the C-2–C-3 double bond plane as suggested by ab initio calculations.[‡] Equatorial attack is favorable for 2-cyano-β-D-2-enopyranoside **4** due to the Factors 1 and 4, but alternative attack by the Factor 2. Bulky *tert*-butyl hydroperoxide exclusively attacked from the equatorial side of **4;** however, the stereoselectivity decreased in the case of hydrogen peroxide. On the other hand, both the reagents attacked only from the equatorial side of the corresponding 2-*C*-nitro alkene **36**. The difference observed in the epoxidation of **4** and **36** with hydrogen peroxide should be caused by a different effect of Factor 3 (the presence or absence of $A^{(1,3)}$ strain). As expected from the Factor 3, axial attack of hydrogen peroxide is higher in 1,5-anhydro cyano alkene **16** than in 1,5-anhydro nitro alkene **38**; the ratio of axial and equatorial attack became 7:1 and ~1:1.7 in **16** and **38**, respectively. Thus the latter two examples should indicate an important role of the $A^{(1,3)}$ strain (Factor 3) to determine the approaching direction of hydroperoxide anion.

3. Experimental

3.1. General methods

Melting points are uncorrected. Optical rotations were determined with a Horiba High Sensitive Polarimeter (SEPA-200). ^{1}H NMR spectra were recorded at 270 MHz (JNM-EX270) or at 400 MHz (Bruker Advance 400) in $CDCl_3$ with Me_4Si as the internal standard. The integration values in the NOE difference spectra are roughly estimated, because measurement conditions were not completely optimized. IR spectra were recorded for the compounds in KBr pellets. The reaction mixtures were dried over $MgSO_4$ and evaporated under diminished pressure. Column chromatography was conducted on silica gel (Wakogel C-300).

[‡] Ab initio calculations (B3LYP/6-31+G*)[16] indicate that the nitro group deviates from the double-bond plane by 13°, probably to reduce repulsion between O-1 and the oxygen atom of the nitro group [$A^{(1,2)}$ strain].[5] As a result the nitro group should suppress the axial attack of a bulky *tert*-butyl hydroperoxide.

3.2. Preparation of methyl 4,6-*O*-benzylidene-2-*C*-cyano-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3)

To a solution of 3-nitro olefin **1** (100 mg, 0.34 mmol)[17] in toluene (10 mL) and H_2O (5 mL) was successively added KCN (33 mg, 0.51 mmol), hexadecyltributylphosphonium bromide (4 mg), and AcOH (0.02 mL, 0.35 mmol). After stirring for 4 h at room temperature (~23 °C), **1** was consumed. The mixture was diluted with EtOAc, washed with aq dil HCl, satd aq NaCl, aq $NaHCO_3$, and satd aq NaCl, dried, and evaporated. The resulting crystalline residue was dissolved in CH_2Cl_2 (20 mL), to which Et_3N (0.06 mL, 0.44 mmol) was added. After stirring for 2 h at room temperature, the mixture was diluted with CH_2Cl_2, washed with dil aq HCl, satd aq NaCl, aq $NaHCO_3$, and satd aq NaCl, dried, and evaporated. The residue was chromatographed with toluene to give 67 mg (72%) of **3**, which was identified by ^{1}H NMR data.[8]

3.3. Preparation of methyl 4,6-*O*-benzylidene-2-*C*-cyano-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (4)

Similar treatment of an ice-cooled solution (0–6 °C) of 3-nitroolefin **2** (30 mg, 0.10 mmol)[18] with KCN (8 mg, 0.12 mmol) for 2 h, followed by similar treatment with Et_3N, gave 24 mg (86%) of **4**, the ^{1}H NMR of which matched those reported.[9]

3.4. Preparation of 4,6-*O*-benzylidene-3-*C*-cyano-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (14)

3.4.1. Methyl 4,6-*O*-benzylidene-3-*C*-cyano-3-deoxy-α-D-altropyranoside (8). To a solution of Et_3Al (15% in toluene, 7.0 mL, 7.68 mmol) in THF (31 mL) was added HCN (0.94 M in THF, 8.1 mL) under an N_2 atmosphere. To the mixture was slowly added a solution of **5** (1 g, 3.78 mmol) in THF (15 mL). After stirring for 20 h, the mixture was slowly added to ice-cooled 2 M aq NaOH (5 mL) and then extracted with $CHCl_3$. The extracts were washed with aq NaCl, dil aq HCl, aq NaCl, aq $NaHCO_3$, and aq NaCl, dried, and evaporated. The residue was chromatographed with 50:1 (v/v), $CHCl_3$–MeOH to give unreacted starting material **5** (400 mg, 40%) and then the *altro* product **8** (350 mg, 32%). The product was used directly in the next step.

3.4.2. Preparation of 4,6-*O*-benzylidene-3-*C*-cyano-3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (14). Davison and Guthrie[10] prepared the corresponding cyano olefin **14** after epimerization at C-3, followed by *p*-bromophenylsulfonylation and elimination in 27% yield (overall yield from **5**). However, the following modified method gave **14** in higher yield.

To a solution of a crude **8** (50 mg, 0.17 mmol) in THF (4 mL) was added Et_3N (0.02 mL, 0.15 mmol) at −20 °C. To the mixture was added dropwise a solution of MsCl (0.016 mL, 0.21 mmol). The mixture was stirred for 1.5 h, diluted with $CHCl_3$ and washed successively with dil aq HCl, aq NaCl, aq $NaHCO_3$, and aq NaCl. The organic phase was dried, and evaporated. The residue was dissolved in $CHCl_3$ (5 mL) and cooled to −30 °C, to which was added DBU (0.04 mL, 0.26 mmol). The mixture was stirred for 2 h at −30 °C, quenched with dil HCl at −30 °C and then extracted with $CHCl_3$. The extracts were successively washed with dil aq HCl, aq NaCl, aq $NaHCO_3$, and aq NaCl, dried, and evaporated. The residue was chromatographed with toluene to give 45.5 mg (97%) of **14** mp 214–214.5 °C, lit.[10] 213–214 °C. The ^{1}H NMR data for the product was identical with those reported.[10]

3.5. Preparation of methyl 4,6-*O*-benzylidene-3-*C*-cyano-3-deoxy-β-D-altropyranoside (9)

Similar treatment of **6** (300 mg, 1.14 mmol)[19] with Et_3Al (15% in toluene, 4.1 mL, 4.55 mmol) and HCN (0.64 M in THF, 7.1 mL) gave unreacted starting material **6** (120 mg, 40%) and then *altro* product **9** (135 mg, 41%), after column chromatography eluting with a gradient of 50:1 to 30:1 (v/v), toluene–EtOAc.

Physicochemical and spectral data for **9**: mp 154–156 °C (*i*-PrOH); $[\alpha]_D^{25}$ +6.2 (*c* 0.7, $CHCl_3$); *v* 3480 (OH) and 2245 cm^{-1} (CN); ^{1}H NMR: δ 4.83 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.16 (br t, 1H, $J_{2,3}$ 3.0, $J_{2,OH}$ 1.3 Hz, H-2), 3.51 (dd, 1H, $J_{3,4}$ 5.0 Hz, H-3), 4.11 (dd, 1H, $J_{4,5}$ 9.2 Hz, H-4), 3.90 (td, $J_{5,6a}$ 9.6, $J_{5,6e}$ 4.3 Hz, H-5), 3.83 (t, 1H, $J_{6a,6e}$ 9.6 Hz, H-6a), 4.37 (dd, 1H, H-6e), 5.57 (s, 1H, PhCH), 2.66 (d, 1H, OH), and 3.60 (s, 3H, OMe). Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.84; H, 6.01; N, 4.75.

3.6. Methyl 4,6-*O*-benzylidene-3-*C*-cyano-3-deoxy-2-*O*-methanesulfonyl-β-D-altropyranoside (12)

To a solution of **9** (20 mg, 0.069 mmol) in THF (2 mL) was added Et_3N (0.02 mL, 0.14 mmol) at −20 °C, followed by the dropwise addition of a solution of MsCl (0.008 mL, 0.10 mmol) in THF (0.1 mL). After 3 min, the mixture was diluted with $CHCl_3$, and the organic phase was washed with dil aq HCl, aq NaCl, aq $NaHCO_3$, and aq NaCl, dried, and evaporated. The residue was chromatographed to give the mesylate **12** (25 mg, 99%): mp 160–161 °C (*i*-PrOH); $[\alpha]_D^{25}$ −21.1 (*c* 0.7, $CHCl_3$); *v* 2255 cm^{-1} (CN); ^{1}H NMR: δ 4.92 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.98 (dd, 1H, $J_{2,3}$ 3.0 Hz, H-2), 3.67 (dd, 1H, $J_{3,4}$ 5.0 Hz, H-3), 4.09 (dd, 1H, $J_{4,5}$ 9.2 Hz, H-4), 3.94 (td, 1H, $J_{5,6a}$ 9.9, $J_{5,6e}$ 4.3 Hz, H-5), 3.86 (t, 1H, $J_{6a,6e}$ 9.5 Hz, H-6a), 4.39 (dd, 1H, H-6e), 5.59 (s, 1H, PhCH), 3.60 (s, 3H, OMe), and 3.14 (s, 3H, Ms).

Anal. Calcd for $C_{16}H_{19}NO_7S$: C, 52.03; H, 5.18; N, 3.79; S, 8.68. Found: C, 51.85; H, 5.40; N, 3.75; S. 8.60.

3.7. Methyl 4,6-*O*-benzylidene-3-*C*-cyano-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (15)

Similar treatment of mesylate **12** (20 mg, 0.054 mmol) with DBU (0.012 mL, 0.08 mmol) employed for preparation of **14** afforded cyano olefin **15** (15 mg, ~100%) after column chromatography eluting 50:1 to 30:1 toluene–EtOAc; mp 167–167.5 °C (*i*-PrOH); $[\alpha]_D^{25}$ −34.7 (*c* 0.8, $CHCl_3$); *v* 2230 cm^{-1} (CN); ^1H NMR (C_6D_6): δ 4.49 (dd, 1H, $J_{1,2}$ 1.7, $J_{1,4}$ 3.0 Hz, H-1), 5.72 (dd, 1H, $J_{2,4}$ 2.3 Hz, H-2), 3.62 (td, 1H, $J_{4,5}$ 8.3 Hz, H-4), 3.27 (m, 1H, $J_{5,6a}$ 9.9, $J_{5,6e}$ 4.3 Hz, H-5), 3.38 (t, 1H, $J_{6a,6e}$ 9.9 Hz, H-6a), 3.97 (dd, 1H, H-6e), 5.16 (s, 1H, PhCH), and 3.06 (s, 3H, OMe). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.81; H, 5.40; N, 4.95.

3.8. 1,5-Anhydro-4,6-*O*-benzylidene-3-*C*-cyano-3-deoxy-D-altritol (10)

Similar treatment of **7** (500 mg, 2.13 mmol)[20] with Et_3Al (15% in toluene, 4.0 mL, 4.28 mmol) and HCN (0.94 M in THF, 4.6 mL, 4.28 mmol) for 20 h, followed by column chromatography eluting with 20:1 (v/v), toluene–EtOAc to give unreacted starting material **7** (120 mg, 24%) and then *altritol* **10** (335 mg, 60%): mp 117–118 °C (toluene–hexane); $[\alpha]_D^{25}$ +47.5 (*c* 0.8, $CHCl_3$); *v* 3480 (OH) and 2245 cm^{-1} (CN); ^1H NMR (C_6D_6, 400 MHz): δ 3.44 (dd, 1H, $J_{1a,1e}$ 13.0, $J_{1a,2}$ 1.4 Hz, H-1a), 3.25 (dt, 1H, $J_{1e,2} = J_{1e,3}$ 1.6 Hz, H-1e), 3.31 (br s, 1H, H-2), 2.76 (m, 1H, H-3), 3.71 (dd, 1H, $J_{3,4}$ 4.9, $J_{4,5}$ 9.5 Hz, H-4), 3.63 (ddd, $J_{5,6a}$ 9.7, $J_{5,6e}$ 4.9 Hz, H-5), 3.39 (br t, 1H, $J_{6a,6e}$ 10.0 Hz, H-6a), 4.05 (dd, 1H, H-6e), 5.20 (s, 1H, PhCH), 1.43 (d, 1H, $J_{2,OH}$ 4.9 Hz, OH). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.58; H, 5.64; N, 5.40.

3.9. 1,5-Anhydro-4,6-*O*-benzylidene-3-*C*-cyano-2,3-dideoxy-β-D-*erythro*-hex-2-enitol (16)

Similar mesylation of **10** (70 mg, 0.27 mmol) with MsCl (0.031 mL, 0.40 mmol) and Et_3N (0.094 mL, 0.68 mmol) for 30 min, as employed for the preparation of **12** gave mesylate **13**, which was found to be labile on silica gel. Compound **13** was converted to cyano olefin **16** by treatment with DBU (0.05 mL, 0.33 mmol) under the same conditions employed for **14**. Compound **16** (52 mg, 80% yield) was obtained after column chromatography: mp 92–93 °C (*i*-PrOH); $[\alpha]_D^{25}$ −47.3 (*c* 0.9, CH_2Cl_2); *v* 2220 cm^{-1} (CN); ^1H NMR: δ 4.41–4.44 (m, 2H, H-1a, H-1e), 6.66 (q, 1H, $J_{1a,2} = J_{1e,2} = J_{2,4}$ 2.6 Hz, H-2), 4.24 (m, 1H, $J_{1a,4} = J_{1e,4}$ 3.0, $J_{4,5}$ 7.9 Hz, H-4), 5.52 (ddd, 1H, $J_{6,6a}$ 10.6, $J_{5,6e}$ 4.6 Hz, H-5), 3.80 (t, 1H, $J_{6a,6e}$ 10.6 Hz, H-6a), 4.34 (dd, 1H, H-6e), and 5.65 (s, 1H, PhCH). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.40; H, 5.10; N, 5.72.

3.10. Typical procedure for epoxidation of cyano olefin with hydrogen peroxide; epoxidation of 3

3.10.1. Method A. To a solution of cyano olefin **3** (20 mg, 0.10 mmol) in 1,4-dioxane (1 mL) was added 30% aq H_2O_2 (0.2 mL) and M NaOH (0.2 mL). After stirring for 30 min at room temperature, the mixture was diluted with EtOAc, and the organic phase was washed with dil aq HCl, aq NaCl, aq $NaHCO_3$, and aq sodium thiosulfate, dried, and evaporated. The crystalline residue was chromatographed with 2:1 (v/v), hexane–EtOAc to give 4.4 mg (13%) of amide **17** with the *manno* configuration and 27 mg (80%) of **18** with the *allo* configuration. Physicochemical and spectral data for **17**: mp 222–223°C (*i*-PrOH); $[\alpha]_D^{25}$ +61.2 (*c* 0.5, $CHCl_3$); *v* 3350, 1680 cm^{-1} ($CONH_2$); ^1H NMR($CDCl_3$, 400 MHz, see Table 1): ^1H NMR (C_6D_6, 400 MHz): δ 4.71 (s, 1H, H-1), 3.75 (s, 1H, H-3), 3.49 (d, 1H, $J_{4,5}$ 9.6 Hz, H-4), 3.69 (td, 1H, H-5), 3.37 (t, 1H, $J_{5,6a} = J_{6a,6e}$ 10.3 Hz, H-6a), 3.97 (dd, 1 H, $J_{5,6e}$ 4.4 Hz, H-6e), 5.14 (s, 1H, PhCH), 2.86 (s, 3H, OMe). Correlation was observed between H-1 and OMe and between PhCH and H-4 as well as H-6a in the NOESY spectrum. Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.73; H, 5.41; N, 4.72. Physicochemical and spectral data for **18**: mp 244–246 °C (*i*-PrOH), $[\alpha]_D^{25}$ +124 (*c* 0.6, $CHCl_3$); *v* 3350, 1660 cm^{-1} ($CONH_2$). For ^1H NMR data see Table 1. Correlation was observed between H-1 and OMe and between PhCH and H-4 as well as H-6a in the NOESY spectrum. Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.62; H, 5.49; N, 4.28.

3.10.2. Method B. To a solution of **3** (100 mg, 0.37 mmol) in 1,4-dioxane (5 mL) was added 30% aq H_2O_2 (0.3 mL) and M NaOH (0.3 mL). After stirring for 10 min at room temperature, the mixture was similarly worked up to give a crystalline residue that was chromatographed with 100:1 (v/v), toluene–EtOAc to afford 7 mg (7%) of the cyano epoxide having the *allo* configuration **19** and starting material **3** (~90%). Physicochemical and spectral data for **19**: mp 168–169 °C (*i*-PrOH); $[\alpha]_D^{25}$ +102.2 (*c* 0.5, $CHCl_3$); *v* 2240 cm^{-1} (CN); in ^1H NMR (C_6D_6, 400 MHz, Table 1) correlation was observed between H-1 and OMe and between PhCH and H-4 as well as H-6a in the NOESY spectrum. The signals of H-1 (s, 1H, 5.07) and PhCH (s, 1H, 5.56) in $CDCl_3$ (400 MHz) were assigned by the 1D-NOESY spectrum by irradiation at OMe (s, 3H, 3.53). Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.29; H, 5.01; N, 4.92.

3.10.3. Method C. To a dispersion of **19** (5 mg) in 1,4-dioxane (0.25 mL) with H_2O_2 (0.05 mL), was added M NaOH (0.05 mL) and the solution was stirred for 30 min at room temperature. After the work-up compound **18** was exclusively formed as judged from the ^{1}H NMR spectrum.

3.11. Typical procedure for epoxidation of cyano olefins with *tert*-butyl hydroperoxide; epoxidation of 3

To a solution of **3** (54 mg, 0.20 mmol) in 1,4-dioxane (3.5 mL) was added ~70% aq *tert*-BuOOH (0.2 mL) and M NaOH (0.2 mL). After stirring for 3 h at room temperature, the mixture was diluted with EtOAc, and the organic phase was washed with dil aq HCl, aq NaCl, aq $NaHCO_3$, aq sodium thiosulfate, and satd aq NaCl, dried, and evaporated. The crystalline residue was chromatographed with 2:1 (v/v), hexane–EtOAc to give 22 mg (38%) of the cyano epoxide with *manno* configuration **20** and the amide with *manno* configuration **17** (5 mg, 8%) and *allo* configuration **18** (24 mg, 40%). Physicochemical and spectral data for **20**: mp 228–230 °C (*i*-PrOH); $[\alpha]_D^{25}$ +0.5 (*c* 0.6, CH_2Cl_2); *v* 2240 cm^{-1} (CN). For ^{1}H NMR data see Table 1. Correlation was observed between H-1 and OMe and between PhCH and H-4 as well as H-6a in the NOESY spectrum. Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.39; H, 4.99; N, 4.65.

Similar treatment of **20** (17 mg, mmol) with 30% aq H_2O_2 (0.2 mL) and M NaOH (0.2 mL) for 30 min at room temperature afforded in almost quantitative yield amide **17** having the *manno* configuration.

3.12. The reaction of methyl 4,6-*O*-benzylidene-2-*C*-cyano-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (4) with hydrogen peroxide

3.12.1. Method A. Similar epoxidation of **4** (30 mg, 0.11 mmol) with 30% aq H_2O_2 (0.2 mL) in the presence of M NaOH (0.2 mL) for 30 min gave a mixture, from which 10 mg (30%) of amide **21** with the *manno* configuration and 20 mg (59%) of **22** with the *allo* configuration were separated by column chromatography eluting with 5:1 (v/v), toluene–EtOAc. Physicochemical and spectral data for **21**: mp 236–237 °C (*i*-PrOH), $[\alpha]_D^{25}$ −49.5 (*c* 0.5, CH_2Cl_2); *v* 3370, 1638 cm^{-1} ($CONH_2$). For ^{1}H NMR data see Table 1. The signals of H-1 and PhCH were confirmed by a 1D-NOESY spectra irradiated at the PhCH signal. Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.80; H, 5.39; N, 4.30. Physicochemical and spectral data for **22**: mp 175–176.5 °C (*i*-PrOH), $[\alpha]_D^{25}$ −32.7 (*c* 0.6, $CHCl_3$); *v* 3420, 1670 cm^{-1} ($CONH_2$). For ^{1}H NMR data see Table 1. Correlation was observed between H-1 and OMe as well as H-5 and between PhCH and H-4 as well as H-6a in the NOESY spectrum. Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.42; H, 5.71; N, 4.66.

3.12.2. Method B. Similar reaction of **4** (100 mg, 0.36 mmol) for 5 min and the same workup afforded a residue, which was chromatographed with 5:1, 2:1, and 1:2 (v/v), hexane–EtOAc to give a mixture of **4**, **26**, and **27** and that of **21**, **22**, **23**, and unknown compounds (not completely purified). Thus the fraction contaminated the unknown compound, therefore, estimation of yields was abandoned. Peroxide **23** crystallized from the above mixture by the use of EtOAc was purified by column chromatography with 2:1 (v/v), hexane–EtOAc.; mp 175–178.5 °C (EtOAc); $[\alpha]_D^{24}$ −175 (*c* 0.03, $CHCl_3$); *v* 3326 (OH), 2253 cm^{-1} (CN); ^{1}H NMR (400 MHz): δ 4.66 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 3.13 (dd, 1H, $J_{2,3}$ 10.9 Hz, H-2), 4.37 (dd, 1H, $J_{3,4}$ 9.9 Hz, H-3), 3.83 (dd, 1H, $J_{4,5}$ 9.4 Hz, H-4), 3.49 (ddd, 1H, H-5), 4.39 (dd, 1H, $J_{5,6e}$ 4.9, $J_{6a,6e}$ 10.3 Hz, H-6e), 3.82 (dd, 1H, $J_{5,6a}$ 10.0 Hz, H-6a), 5.58 (s, 1H, PhCH), 8.43 (s, 1H, –OOH), 3.61 (s, 3H, OMe). Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.33; H, 5.68; N, 4.34.

To hydroperoxide **23** (5 mg, 0.016 mmol) in 1,4-dioxane (0.22 mL) was added 70% of *tert*-BuOOH (0.03 mL) and M NaOH (0.03 mL), and the mixture was monitored by TLC. Even after 10 h starting material still remained; therefore, the same amount of *tert*-BuOOH and M NaOH was added. After 24.5 h, similar workup gave a residue, that was shown by ^{1}H NMR spectroscopy to be compound **21**.

3.13. The reaction of methyl 4,6-*O*-benzylidene-2-*C*-cyano-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (4) with *tert*-butylperoxide and related reactions

3.13.1. Method A. Similar epoxidation of 4 (30 mg, 0.11 mmol) in 1,4-dioxane (1.5 mL) with ~70% aq *tert*-BuOOH (0.2 mL) in the presence of M NaOH (0.2 mL) for 6.5 h gave a crystalline residue that was chromatographed with 5:1 (v/v), toluene–EtOAc to give 33 mg (98%) of **21**.

3.13.2. Method B. Similar reaction of **4** (100 mg, 0.36 mmol) for 5 min, followed by the same workup, gave a mixture. The same reaction was repeated and the residues were combined and then chromatographed with 4:1, 2:1 (v/v), hexane–EtOAc to give a mixture of **4**, **24**, and **26** as the first-running fraction and then **21** (36%) and **25** (34%). The yields of **4** (3%), **24** (22%), **26** (4%) were calculated by integration of their characteristic signals in the ^{1}H NMR spectrum of the mixture. Physicochemical and spectral data for **25**: amorphous, $[\alpha]_D^{24}$ −240 (*c* 0.07, $CHCl_3$); *v* 2252 cm^{-1} (CN); ^{1}H

NMR (400 MHz): δ 4.55 (d, 1H, $J_{1,2}$ 2.2 Hz, H-1), 3.85 (dd, 1H, $J_{2,3}$ 5.0 Hz, H-2), 4.37 (dd, 1H, $J_{3,4}$ 10.2 Hz, H-3), 3.92 (dd, 1H, $J_{4,5}$ 10.1 Hz, H-4), 3.46 (ddd, 1H, H-5), 4.36 (dd, 1H, $J_{5,6e}$ 4.8, $J_{6a,6e}$ 10.6 Hz, H-6e), 3.92 (dd, 1H, $J_{5,6a}$ 9.8 Hz, H-6a), 5.60 (s, 1H, PhCH), 3.58 (s, 3H, OMe), 1.28 (s, 9H, *tert*-Bu). Anal. Calcd for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.76; H, 7.11; N, 3.66.

3.13.3. Partial purification of compound 24. Complete purification of peroxide **24** having the *gluco* configuration was not accomplished, but the NMR data of almost pure **24** was as follows. ^{1}H NMR (400 MHz): δ 4.62 (d, 1H, $J_{1,2}$ 8.7 Hz, H-1), 3.25 (dd, 1H, $J_{2,3}$ 10.6 Hz, H-2), 4.27 (dd, 1H, $J_{3,4}$ 9.3 Hz, H-3), 3.84 (dd, 1H, $J_{4,5}$ 9.6 Hz, H-4), 3.43 (ddd, 1H, H-5), 4.38 (dd, 1H, $J_{5,6e}$ 4.9, $J_{6a,6e}$ 10.4 Hz, H-6e), 3.81 (dd, 1H, $J_{5,6a}$ 10.3 Hz, H-6a), 5.55 (s, 1H, PhCH), 3.60 (s, 3H, OMe), 1.29 (s, 9H, *tert*-Bu).

3.13.4. Epoxidation of 24 to 21. To almost pure **24** (12 mg) (obtained by after several fractional crystallizations) in 1,4-dioxane (0.5 mL) was added 70% *tert*-BuOOH (0.073 mL) and M NaOH (0.073 mL). The mixture was stirred at room temperature for 6.5 h. Similar workup afforded a residue, of which NMR spectroscopy showed the presence of a small amount of starting material **24**. Therefore, the same treatment of the residue was repeated again to give **21** in almost quantitative yield.

3.13.5. Conversion of 25 to 21. To a solution of **25** (6 mg), the 2-epimer of **24**, in 1,4-dioxane (0.25 mL) were added 70% *tert*-BuOOH (0.036 mL), and M NaOH (0.036 mL) and the mixture was stirred at room temperature for 6.5 h. Similar workup afforded a residue, that was shown by NMR spectroscopy to be **21**, together with traces of **24**–**26.**

3.13.6. Epoxidation of 4 with *m*-chloroperoxybenzoic acid. To a solution of **4** (50 mg, 0.18 mmol) in 1,4-dioxane (2.5 mL) was added 70% *m*-chloroperoxybenzoic acid (MCPBA) (135 mg) and M NaOH (0.64 mL), and the mixture was stirred at room temperature for 4 h. Similar workup afforded a residue (56 mg), that was shown by NMR spectroscopy to be a 4.8:2.3:1 mixture of **26**:**27**:**4**. The mixture was dissolved in EtOAc, from which the cyano epoxide **26** (12 mg) was crystallized: mp 200 °C (dec) (EtOAc); $[\alpha]_D^{25}$ −32 (*c* 0.1, $CHCl_3$). The absorption band of CN was not detected in the IR spectrum. For ^{1}H NMR data see Table 1. Correlation was observed between H-1 and OMe and between H-1 and H-5 in the NOESY spectrum. Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.34; H, 5.50; N, 4.63.

Although purification of alternative cyano epoxide **27** was not accomplished, its ^{1}H NMR (400 MHz) see Tables 1 and 3.

3.14. The reaction of methyl 4,6-*O*-benzylidene-3-*C*-cyano-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (14) with *tert*-butyl hydroperoxide

Similar epoxidation of **14** (28 mg, 0.10 mmol) with *tert*-BuOOH (0.1 mL) in the presence of a drop of M NaOH for 20 min afforded a crystalline residue that was chromatographed with toluene to give 28 mg (94%) of cyanoepoxide **29**: mp 185–186.5 °C (*i*-PrOH); $[\alpha]_D^{25}$ +87.2 (*c* 0.7, CH_2Cl_2); ν 2310 cm^{-1} (CN); ^{1}H NMR (400 MHz): δ 4.90 (s, 1H, H-1), 3.60 (s, 1H, H-2), 3.70–3.82 (m, 3H, H-4, H-5, H-6a), ~4.28 (m, 1H, H-6e), 3.48 (s, 3H, OMe), and 5.62 (s, 1H, PhCH). Correlation was observed between H-1 and OMe in the NOESY spectrum. For ^{1}H NMR data (C_6D_6, 400 MHz) see Table 1. Correlation was observed between H-1 and OMe and between PhCH and H-4 as well as H-6a in the NOESY spectrum. Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.55; H, 4.98; N, 4.88.

3.15. The reaction of methyl 4,6-*O*-benzylidene-3-*C*-cyano-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (14) with hydrogen peroxide

Similar treatment of **14** (30 mg, 0.11 mmol) with 30% aq H_2O_2 (0.2 mL) in the presence of a drop of M NaOH for 2 h, followed by addition of H_2O, gave a precipitate. The precipitate was dried over P_2O_5 to give 25 mg (74%) of carbamoyl epoxide **28** (amorphous). Compound **28** was barely soluble in common organic solvents, and its purification by recrystallization was not accomplished. Its ^{1}H NMR spectrum was obtained after repeated accumulations. The *manno* structure was assigned by the transformation of **29** into amide **28** as follows.

To a solution of **29** (10 mg, 0.04 mmol) in 1,4-dioxane (2 mL) was added 30% H_2O_2 (0.1 mL) and a drop of M NaOH. After stirring for 30 min, similar workup gave 10 mg (94%) of **28**, ^{1}H NMR spectrum of which was identical with that of an authentic sample. For ^{1}H NMR spectral data (400 MHz, $CDCl_3$) see Tables 1 and 3.

3.16. The reaction of methyl 4,6-*O*-benzylidene-3-*C*-cyano-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (15) with hydrogen peroxide

Similar epoxidation of **15** (10 mg, 0.037 mmol) with aq H_2O_2 (0.2 mL) in presence of M NaOH (0.2 mL) for 1 h afforded a residue that was chromatographed with 5:1 (v/v), toluene–EtOAc to give the amide having the

allo configuration **30** (11 mg, 98%): mp 211-212 °C (*i*-PrOH); $[\alpha]_D^{25}$ −79.4 (*c* 0.8, $CHCl_3$); *v* 3400, 1680 and 1635 cm^{-1} ($CONH_2$). For ^1H NMR data see Table 1. Correlation was observed between H-1 and OMe, between H-1 and H-2, and between PhCH and H-4 as well as H-6a in the NOESY spectrum. Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.74; H, 5.70; N, 4.56.

Compound **15** (50 mg, 0.18 mmol) in 1,4-dioxane (1 mL) was treated with 30% aq H_2O_2 (0.2 mL) and M NaOH (0.2 mL), and the mixture was stirred for 3 min at room temperature. Similar workup gave a residue that was chromatographed with a gradient of toluene and EtOAc, 100:1 to 5:1, to give the starting material **15** (31 mg, 62%), *gluco* adduct **31** (11 mg, 20%), and amide **30** (10 mg, 18%). Physicochemical and spectral data for **31**: mp 139.5–141 °C (*i*-PrOH); $[\alpha]_D^{25}$ −85.3 (*c* 0.7, $CHCl_3$); *v* 2260 (CN) and 3330 cm^{-1} (OOH); ^1H NMR: δ 4.66 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.04 (dd, 1H, $J_{2,3}$ 10.9 Hz, H-2), 3.31 (t, 1H, $J_{3,4}$ 10.9 Hz, H-3), 3.82 (dd, 1H, $J_{4,5}$ 8.9 Hz, H-4), 3.44 (td, 1H, $J_{5,6a}$ 9.9, $J_{5,6e}$ 5.0 Hz, H-5), 3.80 (t, 1H, $J_{6a,6e}$ 10.6 Hz, H-6a), 4.38 (dd, 1H, H-6e), 5.60 (s, 1H, PhCH), 3.62 (s, 3H, OMe), and 8.94 (br s, 1H, OOH). Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.62; H, 5.64; N, 4.71.

3.17. The reaction of methyl 4,6-*O*-benzylidene-3-*C*-cyano-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (15) with *tert*-butyl hydroperoxide

Similar epoxidation of **15** (10 mg, 0.037 mmol) with *tert*-BuOOH (0.2 mL) in the presence of M NaOH (0.2 mL) for 40 min gave a residue that was chromatographed with 5:1 (v/v) toluene–EtOAc to give 10 mg (89%) of **30**.

3.18. The reaction of 1,5-anhydro-4,6-*O*-benzylidene-3-*C*-cyano-2,3-dideoxy-D-*erythro*-hex-2-enitol (16) with hydrogen peroxide and related reactions

3.18.1. Method A. Similar epoxidation of **16** (20 mg, 0.08 mmol) with H_2O_2 (0.1 mL) in the presence of a drop of M NaOH for 1 h gave a crystalline residue (20 mg) that was chromatographed with toluene to give 6 mg (30%) of glucal **32** and 12 mg (60%) of allal **33**. Physicochemical and spectral data for **32**: mp 127–128.5 °C (*i*-PrOH), $[\alpha]_D^{25}$ −133.3 (*c* 0.3, $CHCl_3$); *v* 2250 (CN) 1642 cm^{-1} (O–C=C); ^1H NMR: δ 6.47 (dd, 1H, $J_{1,2}$ 5.9, $J_{1,3}$ 2.8 Hz, H-1), 4.77 (dd, 1H, $J_{2,3}$ 2.8 Hz, H-2), 3.56 (t, 1H, $J_{3,4}$ 9.5 Hz, H-3), 4.12 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 3.76–3.89 (m, 2H, $J_{5,6a}$ 10.4, H-5, -6a), 4.43 (dd, 1H, $J_{5,6e}$ 5.4, $J_{6a,6e}$ 10.4 Hz, H-6e), and 5.68 (s, 1H, PhCH). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.98; H, 5.64; N, 5.65. Physicochemical and spectral data for **33**: mp 140.5–141 °C (*i*-PrOH); $[\alpha]_D^{25}$ −64.9 (*c* 0.6, $CHCl_3$); *v* 2240 (CN) 1640 cm^{-1} (O–C=C); ^1H NMR: δ 6.49 (dd, 1H, $J_{1,2}$ 5.6, $J_{1,3}$ 1.1 Hz, H-1), 4.83 (t, 1H, $J_{2,3}$ 5.6 Hz, H-3), 3.52 (td, 1H, $J_{3,4}$ 5.6 Hz, H-3), 4.01 (dd, 1H, $J_{4,5}$ 10.1 Hz, H-4), 4.16 (td, 1H, $J_{5,6a}$ 10.4, $J_{5,6e}$ 5.4 Hz, H-5), 3.84 (t, 1H, $J_{6a,6e}$ 10.4 Hz, H-6a), 4.47 (dd, 1H, H-6e), and 5.65 (s, 1H, PhCH). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 68.93; H, 5.18; N, 5.48.

As shown above, the double-bond migration readily occurred; therefore the epoxidation was carried out as follows:

3.18.2. Method B. To a solution of **16** (60 mg, 0.25 mmol) in THF (5 mL) were added 30% aq H_2O_2 (0.2 mL) and M NaOH (0.1 mL) at 0 °C. After stirring for 24 h at 0 °C, 0.2 mL of 30% aq H_2O_2 and 0.1 mL of M NaOH were added to the mixture. This procedure was repeated once again after 24 h. After 4 days (total reaction time), the mixture was diluted with EtOAc, and the organic phase was washed with dil aq HCl, satd aq NaCl, aq $NaHCO_3$, and aq sodium thiosulfate, dried, and evaporated. The crystalline residue (20 mg) was chromatographed with 50:1 (v/v) $CHCl_3$–MeOH to give 50 mg (73%) of epoxide **34** and 7 mg (10%) of epoxide **35**. Physicochemical and spectral data for **34**: mp 234–235.5 °C (*i*-PrOH–EtOH); $[\alpha]_D^{25}$ +11.8 (*c* 0.6, $CHCl_3$); *v* 3360, 1665 cm^{-1} ($CONH_2$). For ^1H NMR data see Table 1. Correlation was observed between H-5 and H-1a in the NOESY spectrum. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.58; H, 5.05; N, 4.78. Physicochemical and spectral data for **35**: mp 218–220 °C (*i*-PrOH–EtOH); $[\alpha]_D^{25}$ +18.9 (*c* 0.4, $CHCl_3$); *v* 3360, 1655 cm^{-1} ($CONH_2$). For ^1H NMR data see Table 1. Correlation was observed between H-5 and H-1a in the NOESY spectrum. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.64; H, 5.15; N, 4.80.

3.18.3. Reaction of 16 with *tert*-butylhydroperoxide. To a solution of **16** (30 mg, 0.12 mmol) in 1,4-dioxane (2.5 mL) were added *tert*-BuOOH (0.2 mL) and M NaOH (0.1 mL) at 0 °C. After stirring at 0 °C for 2 days, the mixture was similarly worked up to give 16 mg (53%) of **32** and 8 mg (27%) of **33**, but there was no evidence for the formation of an epoxide.

3.19. Methyl 2,3-anhydro-4,6-*O*-benzylidene-2-*C*-nitro-β-D-mannopyranoside (37)

3.19.1. Method A. To a solution of **36** (47 mg, 0.16 mmol) in 1,4-dioxane (3.0 mL) were added 30% H_2O_2 (0.3 mL) and then M NaOH (0.3 mL). After stirring for 10 min at room temperature, the mixture was

similarly worked up as described for the preparation of **18** to give 37 mg (75%) of **37**.

3.19.2. Method B. To a solution of **36** (29 mg, 0.10 mmol) in 1,4-dioxane (2 mL) were added 70% *tert*-BuOOH (0.04 mL) and then M aq NaOH (0.04 mL). The mixture was stirred for 20 min. After similar workup, compound **37** was isolated in 92% yield (28 mg); mp 193–196 °C (*i*-PrOH); $[\alpha]_D^{25}$ −55.6 (*c* 1.0, $CHCl_3$); *v* 1565 cm^{-1} (NO_2). For ^1H NMR data see Table 1. Correlation was observed between H-1 and H-5 and between PhCH and H-4 as well as H-6a in the NOESY spectrum. ^1H NMR (CD_3COCD_3): δ 6.03 (s, 1H, H-1), 4.16 (s, 1H, H-3), 3.80 (s, 1H, H-4), 3.82–3.61 (m, 1H, H-5), 3.86 (t, 1H, $J_{5,6a} = J_{6a,6e}$ 9.6 Hz, H-6a), 4.29 (dd, 1H, $J_{5,6e}$ 3.7 Hz, H-6e), 5.72 (s, 1H, PhCH), and 3.61 (s, 3H, OMe). Correlation was observed between H-1 and OMe and between PhCH and H-4 as well as H-6a in the NOESY spectrum. Anal. Calcd for $C_{14}H_{15}NO_7$: C, 54.37; H, 4.89, N, 4.53. Found: C, 54.39; H, 4.62; N, 4.49.

3.20. The reaction of 1,5-anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-D-*erythro*-hex-2-enitol (38) with *tert*-butyl hydroperoxide

To a solution of **38** (20 mg, 0.08 mmol) in 1,4-dioxane (1 mL) were added ~70% aq *tert*-BuOOH (0.1 mL) and then a drop of M NaOH. The mixture was stirred for 2 min at room temperature, and then the reaction was quenched by the addition of dil aq HCl. The mixture was diluted with EtOAc, and the organic phase was washed with aq NaCl (three times), and aq sodium thiosulfate, dried, and evaporated to give a residue (22 mg). The ^1H NMR spectrum of the residue showed that it consisted of 1:1.8 mixture of the epoxides having the *manno* configuration **39** and the *allo* configuration **40**.

When the reaction was prolonged to 1 h, 2,3-anhydro-mannopyranoside **39** was isolated, because during that time **40** had been decomposed. After workup as described above, column chromatography of the residue with 50:1 (v/v) toluene–EtOAc gave **39** in 15% yield; mp 155–155.5 °C (*i*-PrOH); $[\alpha]_D^{25}$ −53.6 (*c* 1.0, $CHCl_3$); *v* 1558 cm^{-1} (NO_2). For ^1H NMR data see Table 1. Correlation was observed between H-5 and H-1 in the NOESY spectrum. Anal. Calcd for $C_{13}H_{13}NO_6$: C, 55.92; H, 4.69; N, 5.02. Found: C, 55.93; H, 4.52; N, 4.82.

3.21. The reaction of 1,5-anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-nitro-D-*erythro*-hex-2-enitol (38) with hydrogen peroxide

To a solution of **38** (20 mg, 0.08 mmol) in 1,4-dioxane (1 mL) were added 30% aq H_2O_2 (0.1 mL) and then a drop of M NaOH. The mixture was stirred for 30 s at room temperature, and then the reaction was quenched by the addition of dil aq HCl. The mixture was diluted with EtOAc, and the organic phase was washed with aq NaCl (three times) and aq sodium thiosulfate, dried, and evaporated to give a residue (21 mg). The ^1H NMR spectrum of the residue showed that it consisted of the epoxides having the *manno* configuration **39** and the *allo* configuration **40** and peroxides having *gluco* **41** and *manno* configuration **42** in the ratio of 1:7.6:4:6 (based on benzylidene methine protons). During the chromatographic separation on silica gel, compound **40** was almost completely decomposed. The product ratio was changed to 1:2.3:0.8:1 after 5 min.

Compounds **40**–**42** could be isolated as follows. The syrup obtained by the reaction for 2 min was dissolved in CH_2Cl_2, and three times its weight of silica gel was added to the solution. The mixture was evaporated until only a small amount of the solvent remained, and then it was chromatographed by the use of 20 times its weight of silica gel, eluting with 50:1 (v/v) toluene–EtOAc to give successively **40**, **41**, and **42**. However, by this method compound **39** could not be isolated due to the overlap with decomposed products generated (probably from **40**). Physicochemical and spectral data for **40**: mp 143–145 °C (toluene–EtOAc), $[\alpha]_D^{25}$ −76.0 (*c* 0.6, $CHCl_3$); *v* 1565 cm^{-1}(NO_2). For ^1H NMR data see Table 1. Correlation was observed between H-5 and H-1a in the NOESY spectrum. Anal. Calcd for $C_{13}H_{13}NO_6$: C, 55.92; H, 4.69; N, 5.02. Found: C, 55.66; H, 4.56; N, 5.02. Physicochemical and spectral data for **41**: mp 87–88 °C (toluene–hexane); $[\alpha]_D^{25}$ +2.0 (*c* 0.5, $CHCl_3$); *v* 3480 (OH), 1558 cm^{-1}(NO_2); ^1H NMR: δ 3.68 (dd, 1H, $J_{1a,1e}$ 11.6, $J_{1a,2}$ 10.2 Hz, H-1a), 4.32 (dd, 1H, $J_{1e,2}$ 5.6 Hz, H-1e), 4.64 (m, 1H, H-2), 5.04 (t, 1H, $J_{2,3} = J_{3,4}$ 10.2 Hz, H-3), 4.13 (t, 1H, $J_{4,5}$ 10.2 Hz, H-4), 3.45 (m, 1H, H-5), 3.77 (t, 1H, $J_{5,6a}$ 10.2, $J_{6a,6e}$ 10.6 Hz, H-6a), 4.40 (dd, 1H, $J_{5,6e}$ 5.0 Hz, H-6e), and 5.55 (s, 1H, PhCH). Anal. Calcd for $C_{13}H_{15}NO_7$: C, 52.53; H, 5.09; N, 4.71. Found: C, 52.41; H, 5.24; N, 4.77. Physicochemical and spectral data for **42**: mp 81–82 °C (toluene–hexane); $[\alpha]_D^{25}$ −86.4 (*c* 0.9, $CHCl_3$); *v* 3320 (OH), 1558 cm^{-1}(NO_2); ^1H NMR: δ 3.66 (dd, 1H, $J_{1a,1e}$ 13.2, $J_{1a,2}$ 1.3 Hz, H-1a), 4.50 (dd, 1H, $J_{1e,2}$ 1.6 Hz, H-1e), 4.82 (dt, 1H, H-2), 4.77 (dd, 1H, $J_{2,3}$ 4.1, $J_{3,4}$ 10.6 Hz, H-3), 4.55 (dd, 1H, $J_{4,5}$ 9.2 Hz, H-4), 3.44 (m, 1H, H-5), 3.88 (t, 1H, $J_{5,6a}$ 10.2, $J_{6a,6e}$ 10.2 Hz, H-6a), 4.37 (dd, 1H, $J_{5,6e}$ 4.9 Hz, H-6e), 5.70 (s, 1H, PhCH), and 8.55 (s, 1H, OOH). Anal. Calcd for $C_{13}H_{15}NO_7$: C, 52.53; H, 5.09; N, 4.71. Found: C, 52.59; H, 5.34; N, 4.67.

3.22. Treatment of 42 with hydrogen peroxide

To a solution of the peroxide having the *manno* configuration **42** (11 mg, 0.04 mmol) in 1,4-dioxane (0.5 mL)

were added 0.05 mL of H_2O_2 and a drop of M NaOH. The mixture was stirred for 2 min. Similar workup of the mixture gave a syrup (11 mg), the ^{1}H NMR of which showed it was a 1:1.3 mixture of **39** and **42**, but gave no evidence for formation of **40** and **41**. For their physicochemical and spectral data see Ref. 9.

3.23. Reactions of 43 with lithium aluminum deuteride

The ^{1}H NMR of **43** (CD_3COCD_3, 400 MHz): δ 5.46 (s, 1H, H-1), 4.49 (s, 1H, H-3), 3.83 (d, 1H, $J_{4,5}$ 9.6 Hz, H-4), 3.95 (ddd, 1H, H-5), 3.85 (t, 1H, $J_{5,6a} = J_{6a,6e}$ 10.1 Hz, H-6a), 4.30 (dd, 1H, $J_{5,6e}$ 4.4 Hz, H-6e), 5.75 (s, 1H, PhCH), and 3.57 (s, 3H, OMe). Correlation was observed between H-1 and OMe and between PhCH and H-4 as well as H-6a in the NOESY spectrum.

To an ice-cooled solution of 2-nitro-α-D-mannopyranoside **43** (29 mg, 0.09 mmol) in THF (2 mL) was added $LiAlH_4$ (16 mg, 0.42 mmol) with stirring under N_2. After stirring for 30 min at room temperature, the mixture was partitioned between water and $CHCl_3$, and the organic layer was evaporated and chromatographed with $CHCl_3$ as an eluent to give 21 mg (84%) of **44**: mp 184–184.5 °C, lit.[21] 186.5–187.5 °C; $[\alpha]_D^{25}$ +118.8 (*c* 1, $CHCl_3$), lit.[21] $[\alpha]_D^{25}$126.9 ± 2. ^{1}H NMR data: δ 4.69 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 3.70 ~ 4.80 (m 3H, H-2, -5, -6a), 1.86 (q, 1H, $J_{2,3a} = J_{3a,3e} = J_{3a,4}$ 11.5 Hz, H-3a), 2.31 (td, 1H, $J_{2,3e} = J_{3e,4}$ 4.6 Hz, H-3e), 3.54 (m, 1H, H-4), 3.45 (dt, 1H, $J_{5,6a}$ 10.2, $J_{5,6e}$ 5.0 Hz, H-5), 3.77 (t, 1H, $J_{6a,6e}$ 10.6 Hz, H-6a), 4.27 (dd, 1H, $J_{6a,6e}$ 10.5, $J_{5,6e}$ 5.6 Hz, H-6e), 5.52 (s, 1H, PhCH), 2.05 (br d, 1H, $J_{2,OH}$ 2.1 Hz, OH), and 3.48 (s, 3H, OMe).

Similar treatment of **43** (26 mg) with $LiAlD_4$ (20 mg) in THF (4 mL) afforded the dideuterio derivative **45**, having the deuterium atom at the axial positions of C-2 and C-3; δ 2.31 (br d, 1H, H-3e).

3.24. Reactions of 46 with lithium aluminum deuteride

The ^{1}H NMR spectrum of **46** (CD_3COCD_3, 400 MHz): δ 6.03 (s, 1H, H-1), 4.36 (br s, 1H, H-3), 4.27 (dd, 1H, $J_{3,4}$ 1.2, $J_{4,5}$ 8.9 Hz, H-4), 3.90 (ddd, 1H, H-5), 3.84 (t, 1H, $J_{5,6a}$ 10.0 Hz, H-6a), 4.32 (dd, 1H, $J_{5,6e}$ 4.2, $J_{6a,6e}$ 9.3 Hz, H-6e), 5.75 (s, 1H, PhCH), and 2.79 (s, 3H, OMe). Correlation was observed between H-1 and OMe and between PhCH and H-4 as well as H-6a in the NOESY spectrum.

In the ^{1}H NMR spectrum of a ~4:1 mixture of **43** and **46** in $CDCl_3$ (400 MHz), the signal due to H-1 of **43** was observed at δ 5.32 and that of **46** at δ 5.98; these signals correlated with OMe signals, respectively, in the NOESY spectrum.

Similar reduction of 2-nitro-α-D-allopyranoside **46** (30 mg, 0.10 mmol) with $LiAlD_4$ (16 mg, mmol) for 30 min gave 23 mg (89%) of **48** (after column chromatography), of which the axial and equatorial positions at C-2 and C-3, respectively, were deuterated; ^{1}H NMR: δ 1.86 (d, $J_{3,4}$ 11.6 Hz, H-3a).

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