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ADDITION OF HYDRAZOIC ACID TO METHYL 6-*O*-BENZOYL-2,3-DIDEOXY-α-D-*glycero*-HEX-2-ENOPYRANOSID-4-ULOSE*

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ABSTRACT

The title compound **4** reacted with hydrazoic acid to give exclusively an adduct having the *threo* configuration, whose structure was established by reduction to the *lyxo* derivatives **8** and **10**. The reaction of **4** with hydrogen peroxide afforded the epoxide **12**, the *lyxo* structure of which was deduced by conversion into the alcohol **13**. Tributylborane also reacted with the enone **4**, giving the adduct **15**, whose configuration was tentatively assigned to be *threo*.

INTRODUCTION

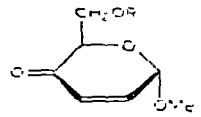
Under conditions of kinetic control, axial nucleophilic attack to conformationally rigid cyclohexene derivatives[1] generally predominates over equatorial attack, whereas various kinds of nucleophiles approach from the equatorial side of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside[2–4] (**1**) and methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-β-D-*erythro*-hex-2-enopyranoside[5]. We have shown that the reaction of **1** with hydrogen cyanide proceeds under kinetic control to give the β-D-glucopyranoside, and have explained this result on the basis of electrostatic repulsion between the entering nucleopile and the C-1–O-1 and C-1–O-5 bonds[2]. Furthermore, the predominance of axial attack[4,6] on the α anomer of **1** was explained in terms of stereoelectronic control and steric hindrance by the glycosidic methoxyl group[2].

To apply these results to the enone system, we have studied the reactions of methyl 6-*O*-benzoyl-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranosid-4-ulose (**4**) with hydrazoic acid and hydrogen peroxide. In the meantime, Gero and co-workers utilized similar reactions of ethyl 2,3-dideoxy-α-D-*glycero*-hex-2-enopyranosid-4-ulose and its 6-*O*-tosyl derivative with sodium azide in aqueous acetic acid for the synthesis of lividosamine[7], nebrosamine[8], purpurosamine[9] C, and sisosamine[9].

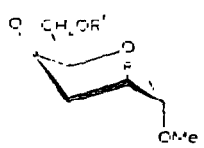
*Stereochemistry of Nucleophilic Addition Reactions. Part IV. For Part III, see ref. 11. Taken from the Master's Dissertation of T. Kawahara, Tokyo Institute of Technology, February 1975.

RESULTS AND DISCUSSION

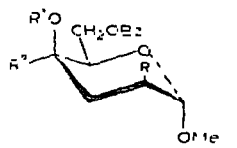
Oxidation of methyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**2**) with manganese dioxide[10] and subsequent benzoylation afforded the 6-benzoate **4** in 38% yield, identical with **4** as obtained by Fraser-Reid *et al.*[10].



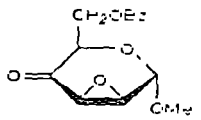
3 R = H
4 R = Bz



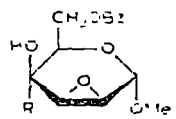
5 R = N_3, R' = Bz
6 R = N_3, R' = H
7 R = NHAc, R' = Bz
15 R = Bu, R' = Bz



8 R = N_3, R' = R" = H
9 R = N_3, R' = H, R" = D
10 R = NHAc, R' = Ac, R" = H
11 R = NHAc, R' = Ac, R" = D



12



13 R = H
14 R = D

Treatment of **4** with hydrazoic acid in chloroform overnight at room temperature afforded methyl 2-azido-6-*O*-benzoyl-2,3-dideoxy-α-D-*threo*-hexopyranosid-4-ulose (**5**) in quantitative yield, as indicated by t.l.c. and n.m.r. spectroscopy, and it was isolated in 81% yield as the (2,4-dinitrophenyl)hydrazone. The i.r. spectrum of **5** showed absorption bands at 2100 (N_3) and 1735 cm^{-1} (C=O). The coupling constants ($J_{1,2}$ 3.0, $J_{2,3_a}$ 5.6, and $J_{2,3_e}$ 5.0 Hz), suggest that the product has the *threo* structure and exists in the $^4C_1$ conformation. The configuration of the azido group was determined by conversion into the alcohol **8**, as described later. Similar treatment of **3** gave the *threo* pyranoside **6** quantitatively. Both azides were fairly unstable, and the reverse reaction occurred gradually upon keeping in a refrigerator and rapidly during column chromatography on silica gel. In the similar reaction of 1-*O*-acetyl-4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranose[11], not only was the *manno*:*gluco* product-ratio sensitive to the solvent used, but also epimerization of the *manno* to the *gluco* isomer was observed in such aprotic, polar solvents as dimethyl sulfoxide[11]. The reaction of **4** with hydrazoic acid, therefore, was examined in various other solvents: it did not proceed in benzene or in 1:5:3 chloroform–tetrahydrofuran–water, even after reaction overnight, but did take place smoothly in chloroform and 1:5 chloroform–tetrahydrofuran. The reaction of **3** with hydrazoic acid was monitored by n.m.r. spectroscopy. As shown in Fig. 1, epimerization was not observed even in dimethyl sulfoxide, and the addition occurred more smoothly in dimethyl

sulfoxide than in chloroform when the same amount of hydrazoic acid was used. It is noteworthy that, when **3** and **4** were treated with deuterium azide prepared from sodium azide and sulfuric acid-d_2 in chloroform–deuterium oxide, the extents of deuteration of H-3a and H-3e were nearly equal.

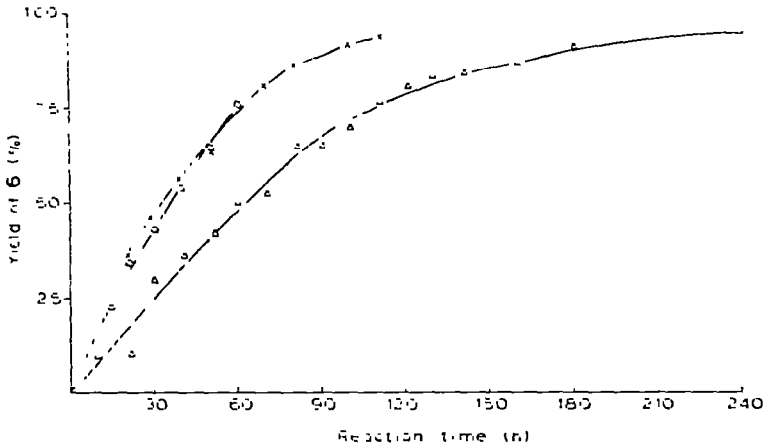


Fig. 1. Relationship between the yield of **6** and the reaction time. The reactions of **3** (0.13 mmol) with hydrazoic acid were performed in an n.m.r. sample-tube at room temperature and monitored by n.m.r. spectroscopy ×, in $CDCl_3$ (0.3 ml, ~1.7M HN_3 solution); ○, in $(CD_3)_2SO$ (0.15 ml) and $CDCl_3$ (0.15 ml, ~1.7M HN_3), and △, in $CDCl_3$ (0.15 ml, ~1.7M HN_3)

When ethyl 2,3-dideoxy-α-D-*glycero*-hex-2-enopyranosid-4-ulose was treated with sodium azide in acetic acid, Gero and co-workers detected by n.m.r. spectroscopy after 5 min only the kinetically controlled, *threo* pyranoside; after 4.5 h, the equilibrium mixture (11:9) of *erythro* pyranoside and *threo* pyranoside was produced. A similar trend was observed in the reaction of **4** with sodium azide in aqueous acetic acid: after 10 min, **5** was formed exclusively (>95%) and, after 24 h, the ratio of **5** and its *erythro* isomer* became 3:4, as shown by n.m.r. spectroscopy.

The configuration of **5** was established by reduction. Catalytic hydrogenation of **5** over 10% Pd/C in ethyl acetate in the presence of acetic anhydride gave the acetamide **7** in 82% yield; it was characterized as the (2,4-dinitrophenyl)hydrazone. Reduction of **5** with sodium borohydride in methanol afforded the crystalline alcohol **8** in 65% yield. In the n.m.r. spectrum of **8**, a 1-proton doublet at δ 4.69 having a splitting of 1.2 Hz was assigned to H-1, indicating the *threo* structure for **5**, but assignment of the C-4 configuration was difficult, because the signals of H-2 and H-4 almost overlapped. The H-4 signal completely disappeared when **5** was reduced with sodium borodeuteride. From these two spectra, the *lyxo* configuration was assigned

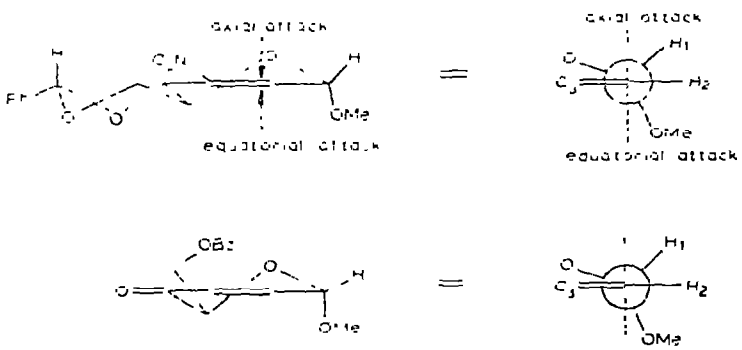
*Although this compound was not isolated, the *erythro* structure was suggested from the i.r. and n.m.r. spectra of the mixture as well as from the fact that treatment of **5** with sodium azide in acetic acid gave an approximately 1:1 mixture of **5** and this compound.

to **8**: $J_{2,3a} = J_{2,3e}$ 3.3, $J_{3a,4}$ and $J_{3e,4} < 3.0$, and $J_{4,5}$ 2.0 Hz. This assignment was confirmed by catalytic hydrogenation of **8** and **9** over 10% Pd/C in the presence of acetic anhydride, followed by *O*-acetylation, leading to **10** and **11**, respectively.

When **4** was treated with hydrogen peroxide in the presence of sodium hydroxide at 0°, a new spot (the epoxide **12**) appeared in t.l.c. After purification by column chromatography, compound **12** was isolated as crystals in 63% yield. Although the isolated yield in this reaction was low, t.l.c. and n.m.r. spectroscopy gave no evidence for formation of the alternative stereoisomer, indicating that this reaction was also highly stereoselective. In the n.m.r. spectrum, a singlet at δ 5.12 was attributable to H-1, but the orientation of the epoxide could not be deduced from this, as Fraser-Reid and Carthy[12] found that the H-1 signals of both ethyl 2,3-dideoxy-2,3-*C*-methylene-6-*O*-trityl-α-D-*ribo*-hexopyranosid-4-ulose and its *lyxo* isomer appeared as singlets. The epoxide **11** was, therefore, reduced with sodium borohydride in methanol to give a mixture (~2:1 by n.m.r. spectroscopy), from which the *talo* isomer **13** was isolated as crystals in 39% yield. In the n.m.r. spectrum of **13**, H-1 resonated at δ 4.87 as a singlet and H-4 at δ 3.99 as a quartet having the spacings $J_{3,4}$ 5.0 and $J_{4,5}$ 3.0 Hz, indicating the *talo* configuration. Assignment of H-4 was ascertained by reduction of **12** with sodium borodeuteride.

Treatment of **4** with tributylborane under an argon atmosphere in the presence of a small amount of air as a radical initiator[13] gave the adduct **15** in 72% yield; it was characterized as the (2,4-dinitrophenyl)hydrazone. The axial orientation at C-2 is tentatively assigned on the basis of data reported by Fraser-Reid and coworkers in the photoaddition of alcohols[14] and dioxolanes[15] to ethyl 2,3-dideoxy-α-D-*glycero*-hex-2-enopyranosid-4-ulose, where the *threo* isomers were formed with a high degree of stereoselectivity.

These results, together with those of Fraser-Reid *et al.*[16] and Gero *et al.*[7–9], showed that axial attack occurred exclusively, or at least predominantly, in both nucleophilic and radical reactions of α-D-hex-2-enopyranosid-4-ulose derivatives. It is noteworthy that the stereoselectivity of the reaction of the enone **4** with hydrazoic acid was higher than that of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-



Scheme 1.

erythro-hex-2-enopyranoside (the α anomer of **1**), where the highest ratio of axial attack to equatorial attack was 8:1 in dimethyl sulfoxide. The difference may be explained as follows; firstly, the enone **4** has no C-4 proton, which would retard the axial attack through 1,3-nonbonded steric interaction; secondly, as shown in Scheme 1, the glycosidic methoxyl group of the enones occupies a closer position on a line perpendicular to the plane of the double bond than that of the nitroalkene, and therefore, the reagent entering from the equatorial side would encounter more-severe steric hindrance in the former than in the latter.

EXPERIMENTAL

General methods. — Melting points were determined in capillaries and are uncorrected. Evaporations were performed under diminished pressure. I.r. spectra were recorded for potassium bromide discs with a Hitachi 215 i.r. spectrophotometer. N m r. spectra were determined either at 100 MHz with a JNM-4H-100 (JEOL) or a Varian T-60 spectrometer in chloroform-*d*, using tetramethylsilane as the internal standard. Column chromatography was conducted on silica gel (C-200 or C-300 Wakogel, Japan). T.l.c. was performed on Kieselgel GF 254.

Methyl 2,3-dideoxy-α-D-glycero-hex-2-enopyranosid-4-ulose (**3**). — The enopyranoside[10] **2** (1.21 g, 7.6 mmol) in chloroform (500 ml) was stirred with activated manganese dioxide (12.2 g) at room temperature. After 3 h, the starting material was no longer present (t.l.c., R_F 0.11, 1:1 benzene–ethyl acetate). The manganese dioxide was filtered off and the filtrate was evaporated to a syrup (R_F 0.25, 0.84 g, 71%) that was pure as indicated by t.l.c. and n.m.r. spectroscopy. The syrup crystallized when refrigerated. Recrystallization from ethanol gave 0.65 g (54%) of **3**; m.p. 82.0–82.5°, $[\alpha]_D^{20}$ +31.2° (*c* 1, chloroform); ν_{max} 3300 (OH) and 1690 cm^{-1} (C=O); n.m.r. data: δ 6.93 (1 H, q, $J_{1,2}$ 3.6, $J_{2,3}$ 10.5 Hz, H-2), 6.13 (1 H, d, H-3), 5.21 (1 H, d, H-1), 4.39 (1 H, t, $J_{5,6}$ 3–4 Hz, H-5), 3.98 (2 H, d, H-6 and H-6'), 3.53 (3 H, s, OMe), and 2.7–3.0 (1 H, OH).

Anal. Calc. for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.35; H, 6.35.

Methyl 6-O-benzoyl-2,3-dideoxy-α-D-glycero-hex-2-enopyranosid-4-ulose (**4**). — To a solution of the crude glyculose **3** (1.58 g, 10 mmol) in dichloromethane (20 ml) was added pyridine (10 ml) at −30°. Benzoyl chloride (2.03 ml, 16.3 mmol) was added dropwise over a period of 1.5 h at −30° with stirring. After being kept for an additional 0.5 h at −30°, the mixture was refrigerated overnight, poured into ice–water (150 ml), and then extracted with dichloromethane. The extract was successively washed with 2M aqueous hydrochloric acid, water, aqueous sodium hydrogencarbonate, and water, dried (sodium sulfate), and evaporated to a syrup. Chromatography of the syrup on silica gel (elution with 10:1 benzene–ethyl acetate) afforded a white solid. Recrystallization from ethanol gave **4** (1.86 g, 71%); m.p. 71–72° (lit.[10] m.p. 70°). $[\alpha]_D^{20}$ −36.7° (*c* 1 chloroform) [lit. −38.5° (*c* 1, chloroform)].

Anal. Calc. for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38. Found: C, 64.02; H, 5.39.

Methyl 2-azido-6-O-benzoyl-2,3-dideoxy-α-D-threo-hexopyranosid-4-ulose (**5**). —

The enone **4** (52.4 mg, 0.2 mmol) was added to a chloroform solution of hydrazoic acid (1 ml, ~1.7M) at room temperature, and the mixture was kept for 18 h, whereupon t.l.c. (9:1 benzene–methanol) showed that all of the starting material (R_F 0.57) had disappeared and a new spot (R_F 0.51) was present. The chloroform was evaporated off to give an n.m.r.-spectroscopically pure syrup (59 mg): n.m.r. data: δ 4.84 (1 H, d, $J_{1,2}$ 3.0 Hz, H-1), 3.94 (1 H, m, $J_{2,3a}$ 5.6, $J_{2,3e}$ 5.0 Hz, H-2), 2.83 (1 H, q, H-3e), and 2.72 (1 H, q, $J_{3a,5} \leq 1$ Hz, H-3a). Attempts to purify the product by column chromatography on silica gel led to the recovery of **4** (75%). The product **5** was isolated as its (2,4-dinitrophenyl)hydrazone in 81% yield; m.p. 154–155°, $[\alpha]_D^{20}$ +43.1° (*c* 1, chloroform).

Anal. Calc. for $C_{20}H_{19}N_7O_8$: C, 49.48; H, 3.95; N, 20.20. Found: C, 49.18; H, 4.00; N, 20.20.

Methyl 2-azido-2,3-dideoxy-α-D-threo-*hexopyranosid-4-ulose* (**6**). — Compound **3** (31.6 mg, 0.2 mmol) was similarly treated with hydrazoic acid to give **6** in quantitative yield; n.m.r. data. δ 5.02 (1 H, d, $J_{1,2}$ 2.8 Hz, H-1), ~4.0 (1 H, m, $J_{2,3a}$ 6.0, $J_{2,3e}$ 5.1 Hz, H-2), ~2.8 (2H, m, H-3e, H-3a). Compound **6** was isolated as its (2,4-dinitrophenyl)hydrazone in 82% yield, m.p. 156–157°, $[\alpha]_D^{20}$ +78.4° (*c* 1, chloroform).

Anal Calc. for $C_{13}H_{15}N_7O_7$: C, 40.95; H, 3.97; N, 25.72. Found: C, 41.43; H, 4.13; N, 25.28.

Methyl 2-acetamido-6-O-benzoyl-2,3-dideoxy-α-D-threo-*hexopyranosid-4-ulose* (**7**). — A solution of **5**, directly prepared from the enone **4** (0.4 mmol) in the way already described, in ethyl acetate (20 ml)–acetic anhydride (300 mg) was hydrogenated in the presence of 10% Pd/C (180 mg). After 2 h, the catalyst was filtered off and the filtrate was evaporated to a syrup that was chromatographed on silica gel with 9:1 benzene–methanol as eluant (in order to remove a first-running, small amount of methyl 6-*O*-benzoyl-2,3-dideoxy-α-D-*glycero*-hexopyranosid-4-ulose, arising from the enone **4**), to give **7** as an almost pure syrup (105 mg, 82%): ν_{max} 1660 and 1560 cm^{-1} (NHAc); n.m.r. data: δ ~4.8 (1 H, d, $J_{1,2}$ 2–3 Hz, H-1), 3.9–4.3 (1 H, m, H-2), 2.87 (1 H, q, $J_{2,3e}$ 3.3 Hz, H-3e), and 2.65 (1 H, q, $J_{2,3a}$ 5.4 Hz, H-3a). Compound **7** was characterized as its (2,4-dinitrophenyl)hydrazone; m.p. 216–217°, $[\alpha]_D^{20}$ +167° (*c* 1, chloroform).

Anal. Calc. for $C_{22}H_{23}N_5O_9$: C, 52.69; H, 4.62; N, 13.97. Found: C, 52.35; H, 4.48; N, 13.97.

Methyl 2-azido-6-O-benzoyl-2,3-dideoxy-α-D-lyxo-*hexopyranoside* (**8**). — The crude azide **5**, prepared from the enone **4** (209.6 mg, 8 mmol), was dissolved in methanol (10 ml), and the solution was cooled to 0°. Sodium borohydride (3 × 100 mg) was added during 30 min at 0° with stirring, and the mixture was then kept for an additional 30 min at room temperature. After a small amount of acetone had been added, the solution was neutralized with dilute acetic acid and then concentrated. The product was extracted with chloroform. The extract was washed with water, dried (sodium sulfate), and evaporated to leave a white solid. Recrystallization from isopropyl alcohol gave 160 mg (65%) of **8**; m.p. 89–90°, $[\alpha]_D^{20}$ +43.8° (*c* 1, chloro-

form); ν_{max} 3540 (OH), 2100 (N_3), and 1720 and 1600 cm^{-1} (OBz); n.m.r. data: δ 4.69 (1 H, d, $J_{1,2}$ 1.2 Hz, H-1), 3.76 (1 H, m, $J_{4,5}$ 2 Hz, H-4), 3.65 (1 H, m, H-2), 2.09 (1 H, d, $J_{2,3e}$ 3.3 Hz, H-3e), and 2.07 (1 H, d, $J_{2,3a}$ 3.3 Hz, H-3a).

Anal. Calc. for $C_{14}H_{17}N_3O_5$: C, 54.72; H, 5.58; N, 13.68. Found: C, 54.98; H, 5.65; N, 13.93.

*Methyl 2-azido-6-O-benzoyl-2,3-dideoxy-3-deuterio-α-*D*-lyxo-hexopyranoside* (**9**). — The crude azide **5** was treated with sodium borodeuteride in methanol and the product was isolated as already described; m.p. 90.5–91.5°.

*Methyl 2-acetamido-4-O-acetyl-6-O-benzoyl-2,3-dideoxy-α-*D*-lyxo-hexopyranoside* (**10**). — A solution of **8** (160 mg, 0.52 mmol) in methanol (20 ml)–acetic anhydride (600 mg) was hydrogenated in the presence of 10% Pd/C (200 mg). After 2 h, the catalyst was filtered off and the filtrate was evaporated to a syrup that was treated with pyridine (1.2 ml)–acetic anhydride (0.8 ml) overnight at room temperature. Conventional isolation gave a white solid. Recrystallization from isopropyl alcohol afforded 112 mg (59%) of **10**; m.p. 121–122°, $[\alpha]_D^{20}$ +18.5° (*c* 1, chloroform); ν_{max} 1742 (OAc), 1721 (OBz), and 1640 and 1540 cm^{-1} (NHAc); n.m.r. data: δ 6.39 (1 H, d, $J_{2,NH}$ 9.5 Hz, NH), 5.13 (1 H, $J_{3,4}$ and $J_{4,5} \leq 5$ Hz, H-4), 4.57 (1 H, d, $J_{1,2}$ 1–2 Hz, H-1), 4.0–4.3 (1 H, m, H-2), and 1.7–2.4 (2 H, H-3a, and H-3e).

Anal. Calc. for $C_{18}H_{23}NO_7$: C, 59.18; H, 6.33; N, 3.83. Found: C, 59.29, H, 6.41; N, 3.89.

*Methyl 2-acetamido-4-O-acetyl-6-O-benzoyl-2,3-dideoxy-3-deuterio-α-*D*-lyxo-hexopyranoside* (**11**). — Compound **9** was hydrogenated in the presence of 10% Pd/C and the product was isolated as already described; m.p. 125–126°.

*Methyl 2,3-anhydro-6-O-benzoyl-α-*D*-lyxo-hexopyranosid-4-ulose* (**12**). — To a solution of **4** (104.8 mg, 0.4 mmol) and aqueous 30% hydrogen peroxide (0.12 ml, 1.2 mmol) in methanol (0.4 ml) was added 6M sodium hydroxide (0.2 ml) dropwise with stirring at 0°. T.l.c. (9:1 benzene–methanol) revealed that almost all of the starting material (R_F 0.57) had disappeared within 10 min and a new spot (R_F 0.61) had appeared. After stirring for an additional 1 h at room temperature, the product was extracted with chloroform. The extract was washed with water, dried (sodium sulfate), and evaporated. The resulting syrup was chromatographed on silica gel with benzene, and the eluate was evaporated to give white crystals (70 mg, 63%) that were pure as determined from elemental analysis, t.l.c., and n.m.r. spectroscopy. Compound **12** was recrystallized from isopropyl alcohol; m.p. 112–113°, $[\alpha]_D^{20}$ +124° (*c* 1, chloroform); ν_{max} 1737 (C=O), 1720 and 1600 cm^{-1} (OBz); n.m.r. data δ 5.12 (1 H, s, H-1), 3.5–3.6 (1 H, d, $J_{2,3}$ 4.5 Hz, H-2), and 3.45–3.55 (1 H, d, H-3).

Anal. Calc. for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.55; H, 5.13.

*Methyl 2,3-anhydro-6-O-benzoyl-α-*D*-talopyranoside* (**13**). — The epoxide **12** (56 mg, 0.2 mmol) was reduced with sodium borohydride as described for the preparation of **8**, affording a white solid (43 mg, 77%). Its i.r. spectrum showed no carbonyl group absorption but a hydroxyl-group band (3490 cm^{-1}) was present and its n.m.r. spectrum revealed that it consisted of two compounds (2:1). The major product (**13**) was isolated by recrystallization from isopropyl alcohol; yield 22 mg

(39%); m.p. 145–146°, $[\alpha]_D^{20}$ +25.3° (*c* 0.76, chloroform); n.m.r. data: δ 4.87 (1H, s, H-1), 4.00 (1H, t, $J_{4,5}$ 3.0 Hz, H-5), 3.99 (1H, q, $J_{3,4}$ 5 Hz, H-4), 3.55 (1H, m, $J_{2,3}$ 3.6 Hz, H-3), 3.17 (1H, d, H-2), and 2.4 (1H, OH).

Anal. Calc. for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 60.13; H, 5.64.

Similar treatment of **12** with sodium borodeuteride gave **14** in 35% yield; m.p. 145–146°.

*Methyl 6-O-benzoyl-2-C-butyl-2,3-dideoxy-α-*D*-threo-hexopyranosid-4-ulose* (**15**). — To a solution of **4** (52.4 mg, 0.2 mmol) in isopropyl alcohol (6 ml)–water (7 μl, 0.4 mmol) was added tributylborane (0.1 ml) with stirring at room temperature under an argon atmosphere. Air (5 ml) was passed into the flask at a rate of 0.5 ml/min. After 4 h, aqueous 30% hydrogen peroxide and aqueous sodium acetate were added to the mixture with stirring, and then manganese dioxide was added after 10 min. The manganese dioxide was filtered off, the filtrate was evaporated, and the product was extracted with chloroform. The extract was washed with water, dried (sodium sulfate), and evaporated to a syrup (72%) that was pure as determined by t.l.c.; n.m.r. data: δ 4.71 (1H, d, $J_{1,2}$ <5 Hz, H-1), 2.36–2.60 (2H, H-3a, H-3e), and 1.8–2.3 (1H, $J_{2,3a}$ 7.1, $J_{2,3e}$ 5.1 Hz, H-2). The product **15** was characterized as its (2,4-dinitrophenyl)hydrazone: m.p. 138–140°, $[\alpha]_D^{20}$ +116.8° (*c* 1, chloroform).

Anal. Calc. for $C_{24}H_{28}N_4O_8$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.40; H, 5.50; N, 11.28.

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