the correlations. Consequently, it was concluded that the carbon-13 chemical shifts could not be satisfactorily correlated with a single-parameter expression.

Experimental Section

The syntheses of the compounds employed in this study have been previously described.[8]

The infrared spectra were recorded on a Perkin-Elmer 567 spectrophotometer in the region of 1800–1600 cm^{-1} with tetrachloromethane and dried chloroform as solvents. For measurement, NaCl cells with path lengths of 0.01, 0.1, 0.5, and 1 cm were used. Uniform concentrations for all compounds were chosen to give an absorption of 70–75%. The C=O stretching frequencies were determined with an accuracy of ±1 cm^{-1}.

Carbon NMR spectra were obtained by employing a JEOL FX-60Q Fourier transform NMR spectrometer operating at a frequency of 15.04 MHz. Data were accumulated on a Texas Instruments 980B computer using 8192 data points over a 4-kHz spectral width to yield a data-point resolution of 0.99 Hz. For noise-decoupled spectra, samples were irradiated by using a pulse width corresponding to 45°, and a 5-s pulse-repetition time was used. For the proton-coupled spectra, a gated pulse sequence was used to obtain NOE intensification of the signals. The NMR samples were prepared by weight as 0.1 M solutions with commercial NMR grade dimethyl-d_6 sulfoxide. The signals are referenced to Me_4Si by giving the most intense solvent signal the value of 39.6 ppm.

The linear free-energy statistical treatment of the data was carried out as previously described.[9]

The lanthanide shift reagent studies on Ia were carried out in $CDCl_3$, for solubility reasons, by using tris(6,6,7,7,8,8,8-heptafluoro-2,2,3,5-tetramethyl-3,5-octanedionato)europium. Shift data were collected at 0, 0.05, 0.1, 0.2, and 0.3 molar equiv of the lanthanide with respect to Ia, and the data reported are a result of extrapolation to a 1:1 complex. The control study with 3-methylthiophene was carried out in the same manner, and no change (less than 0.1 ppm for a 1:1 complex) in chemical shift for any carbon was observed.

Acknowledgment. A.P. thanks the International Research and Exchange Board for support which allowed the completion of this work at Georgia State University.

Registry No. Ia, 14282-78-1; Ib, 14282-65-6; Ic, 54796-49-5; Id, 61854-93-1; Ie, 61854-92-0; If, 61854-96-4; Ig, 61854-94-2; Ih, 54796-50-8; Ii, 61854-95-3; IIa, 19156-50-4; IIb, 25744-99-4; IIc, 61854-98-6; IId, 61855-00-3; IIe, 61854-99-7; IIf, 61855-03-6; IIg, 61855-01-4; IIh, 61854-97-5; IIi, 61855-02-5.

(8) M. Němec, M. Janda, J. Šrogl, and I. Stibor, *Collect. Czech. Chem. Commun.*, **39**, 3527 (1974).

(9) P. J. Duke and D. W. Boykin, *J. Org. Chem.*, **37**, 1436 (1972).

Evidence for Bicyclic Oxonium Ions in the Nitrous Acid Deamination of Benzyl 2-Amino-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosides[1]

Wai-Pan Chan and Paul H. Gross*

Department of Chemistry, University of the Pacific, Stockton, California 95211

Received March 26, 1979

The nitrous acid deamination of conformationally rigid benzyl amino-4,6-*O*-benzylidenedeoxy-D-hexopyranosides was studied: benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (**5**) and benzyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucopyranoside (**4**) in aqueous dioxane both gave some benzyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**2**). Thus, a trans-diaxial arrangement of hydroxyl and amino groups in the ground state does not appear to be an absolute requirement for epoxide formation, although such an arrangement clearly is most conducive to this reaction, as a comparison of yields showed. Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside (**7**) under similar conditions gave, by elimination, benzyl 4,6-*O*-benzylidene-α-D-*erythro*-hexopyrano-3-uloside (**8**) and, by benzyloxy migration, 2-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (**11**). Contrary to expectation, the same products, **8** and **11**, were isolated from the deamination of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**10**) and its α-D-mannopyranoside analogue (**7**). A bicyclic oxonium ion is postulated as an intermediate for the deamination of the α-D-gluco isomer. Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**13**), with nitrous acid, gave benzyl 4,6-*O*-benzylidene-2-deoxy-β-D-*erythro*-hexopyrano-3-uloside (**14**). Here also, a bicyclic oxonium ion appears to be involved. All products isolated in this or earlier work from the deamination of 2-amino-4,6-*O*-benzylidene-D-glucopyranosides can be explained by mechanisms involving bicyclic oxonium ion intermediates. Such intermediates are apparently not involved in the deamination of the manno or altro analogues.

Nitrous acid deamination was used early to study structures of 2-amino-2-deoxy-D-glucose[2,3] and its analogues. Deamination reactions of various amino sugars were reviewed by Williams.[4] Inversion and rearrangement products were reported.[5-9] Nitrous acid deamination was used to cleave hydrolysis-resistant glycosidic linkages[10] by a technique valuable in the elucidation of the structure of heparin.[10-14] Hydrazinolysis followed by nitrous acid deamination of α_1-acid glycoprotein gave acidic and neutral mono- and oligosaccharides.[15]

(1) (a) From the M.S. thesis of Wai-Pan Chan, University of the Pacific, Stockton, CA, 1974. (b) A preliminary version was presented at the 172nd National Meeting of the American Chemical Society, San Francisco, CA, 1976, No. CARB 6. (c) Partial support by the Research Corp. is gratefully acknowledged.

(2) Mills, J. A. *Adv. Carbohydr. Chem.* **1955**, *10*, 1.

(3) Wiggins, L. F. *Nature (London)* **1946**, *157*, 300.

(4) Williams, J. M. *Adv. Carbohydr. Chem.* **1975**, *30*, 9.

(5) Foster, A. B.; Martlew, D. F.; Stacey, M. *Chem. Ind. (London)* **1953**, 825–6.

(6) Egyud, L. G.; Szent-Gyorgyi, A. *Science* **1967**, *155*, 539.

(7) Fischer, E.; Tiemann, F. *Ber Dtsch. Chem. Ges.* **1894**, *27*, 138.

(8) Foster, A. B. *Chem. Ind. (London)* **1955**, 627.

(9) Ledderhose, G. *Z. Physiol. Chem.* **1878**, 2, 213.

(10) Foster, A. B.; Horton, D.; Stacey, M. *J. Chem. Soc.* **1957**, 81–6.

(11) Foster, A. B.; Huggard, A. J. *Adv. Carbohydr. Chem.* **1955**, *10*, 335–68.

(12) Foster, A. B.; Harrison, R.; Inch, T. D.; Stacey, M.; Webber, J. M. *J. Chem. Soc.* **1963**, 2279–87.

(13) Wolfrom, M. L.; Wang, P. Y.; Honda, S. *Carbohydr. Res.* **1969**, *11*, 179.

(14) Cifonelli, J. A.; King, J. *Carbohydr. Res.* **1972**, *21*, 173.

(15) Bayard, B.; Fournet, B. *Carbohydr. Res.* **1976**, *46*, 75.

0022-3263/80/1945-1369$01.00/0

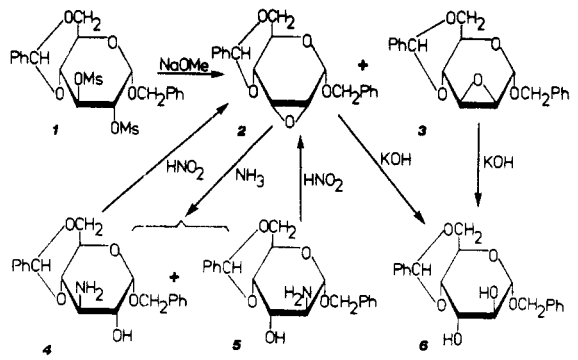

Figure 1. Formation of epoxide **2** by nitrous acid deamination of the two benzyl amino-4,6-*O*-benzylidenedeoxy-D-hexopyranosides **4** and **5**.

Deamination by nitrous acid proceeds via a diazonium ion intermediate either by concerted reaction or by way of a carbonium ion intermediate. The product composition of deamination reactions depends on the reaction pathway.[16] In weakly acidic aqueous media,[17] the diazotizing species were found to be $H_2NO_2^+$ (nitrous acidium ion), N_2O_4 (dinitrogen tetraoxide) and HNO_2 (nitrous acid).

Early evidence for the importance of conformations on the outcome of nitrous acid deamination reactions of cyclohexanol amines came from the work of McCasland[18] and Curtin and Schmuckler.[19] Cherest et al.[20] investigated further the nitrous acid deamination of conformationally "fixed" 4-*tert*-butyl-2-aminocyclohexanols and compared their results to mobile systems. Their results clearly established an anticoplanar conformational requirement for the bonds participating in the deamination step. Less side products were observed in the deamination of the conformationally "fixed" systems than in "mobile" systems. Three major products were identified as a ring-contracted aldehyde, a ketone, and an epoxide. For the interpretation of our results, we found this paradigm, advanced by Cherest, to be more appropriate than the hypotheses formulated in a review paper by Collins[21] which discussed only deaminations of open-chain amino alcohols.

Ring contractions were also found in the nitrous acid deamination of 2-amino-2-deoxy-D-glucose.[22-24] In summary, evidence for concerted mechanisms in nitrous acid deaminations of cyclic amino alcohols is very convincing, and simple carbonium ion intermediates are unlikely. Osawa and Akiya[25] found that the only isolable product of nitrous acid deamination of methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside was 2,5-anhydro-4,6-*O*-benzylidene-D-mannose. This ring contraction was completely explained by the concerted reactions of three coplanar electronic orbitals in the N_2-elimination step of the deamination. Considering also our results for the deaminations of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosides, we postulate here a bicyclic oxonium ion intermediate, which can explain coherently this previously found ring contraction[25] as well as the keto sugar formation and aglycon migration observed by us.

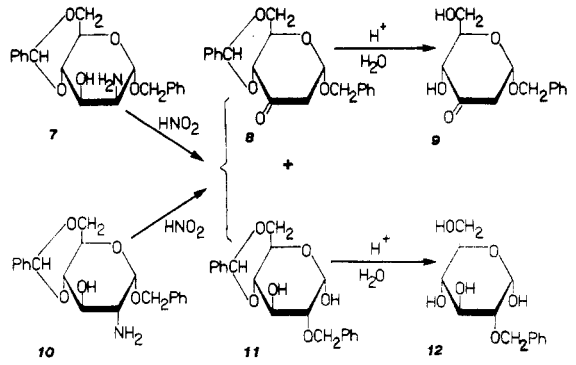

Figure 2. Nitrous acid deamination of two 2-amino sugars **7** and **10**.

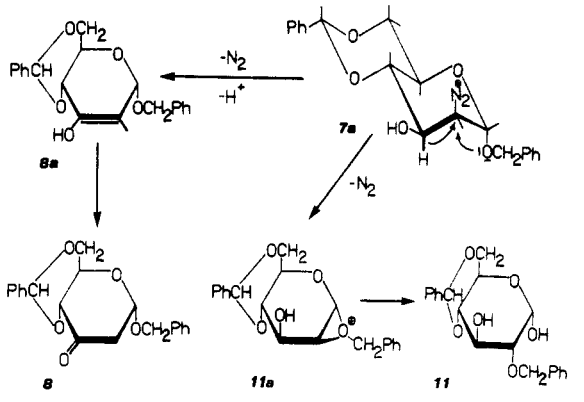

Figure 3. Formation of a keto sugar **8** and a 2-*O*-benzylglucose derivative, **11**, by nitrous acid deamination of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside (**7**).

Discussion

Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (**5**) and a minor amount of its 3-amino-3-deoxy-α-D-gluco analogue (**4**) were obtained by the method of Chiu.[26] The dimesyl compound **1**, prepared by conventional methods, with sodium methoxide gave mainly the allo epoxide **2**. We also succeeded in isolating a minor amount of the isomeric manno epoxide **3** (2% yield) after detecting it as a fast-moving spot on TLC. The structure of **3** was proven by alkaline hydrolysis to the altro derivative **6**, which was also obtained from **2**. The ammonolysis[26] of **2** leads mainly to the 2-amino-α-D-altro isomer **5** as shown in Figure 1. However, from the mother liquor we were able to isolate a small proportion of the 3-amino-α-D-gluco isomer **4**. Both amino alcohols (**4** and **5**) were then subjected to nitrous acid deamination. As was expected, nitrous acid transformed **5** into the epoxy sugar **2** in good yield (65%); however, the postulate of three coplanar bonds in the molecular ground state being absolutely necessary for such epoxide formation[20] must be qualified, since a small yield of the same epoxide (30%) was found for the deamination of **4**.

Yet, as can be seen in the following examples, all other deamination products observed before and in this work may be linked to this postulate. Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranose (**7**) was prepared according to Chiu[26] and subjected to nitrous acid deamination with the result shown in Figure 2. For deaminations, mixtures of 3–2 parts of dioxane with 2–1 parts of citrate buffer of pH 3.5 were found to be optimal, i.e., acidic enough to guarantee a reasonable fast deamination and unpolar enough to minimize cleavage of the 4,6-*O*-

(16) Hughes, E. D.; Ingold, C. K.; Ridd, J. H. *J. Chem. Soc.* **1958**, 82 and prior articles by these authors.
(17) Hughes, E. D.; Ingold, C. K.; Ridd, J. H. *J. Chem. Soc.* **1958**, 88.
(18) McCasland, G. E. *J. Am. Chem. Soc.* **1951**, *73*, 2293.
(19) Curtin, D. Y.; Schmuckler, S. *J. Am. Chem. Soc.* **1955**, *77*, 1105.
(20) Cherest, M.; Felkin, H.; Sicher, J.; Sipos, F.; Tichy, M. *J. Chem. Soc.* **1965**, 2513.
(21) Collins, C. *Acc. Chem. Res.* **1971**, *4*, 315.
(22) Fischer, E.; Andrae, E. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2587.
(23) Tiemann, F. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 118.
(24) Peat, S. *Adv. Carbohydr. Chem.* **1946**, *2*, 37.
(25) Osawa, T.; Akiya, A. *Chem. Pharm. Bull.* **1959**, *7*, 277.

(26) Chiu, T. Doctoral Dissertation, University of the Pacific, Stockton, CA, 1971.

benzylidene group. Also, the dioxane made possible easy dissolution of the organic material. Throughout this paper yields of analytically pure material are quoted. These yields reflect the inevitable loss of de-O-benzylidenated materials to the aqueous phase during extraction.

Compound 7 gave only two major products: benzyl 4,6-O-benzylidene-2-deoxy-α-D-*erythro*-hexopyrano-3-uloside (8, 45%) and 2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranose (11, 26%). Both products were obtained crystalline, and their structures could be unequivocally established. The keto sugar 8 was formed by elimination as shown in Figure 3. The diazonium ion intermediate **7a**, derived from 7, can decompose in two ways, which would both fit the theorem of the concerted reaction of three coplanar orbitals.[20] The diazonium group is anticoplanar with the axial proton at C-3. Concerted elimination of this proton and the nitrogen molecule led to the enol form **8a** which tautomerizes to the keto sugar 8. The keto sugar 8 was also obtained by Tompkins[27] in our laborabory by an independent route.

On the other hand, another mechanism appeared to compete in the deamination of 7, leading to the formation of 2-O-benzyl sugar 11. The anticoplanar axial benzyloxy group participates in the nitrogen ejection. An epoxonium ion, **11a**, will be formed which undergoes an electronically controlled opening at the site of the more stable carbonium ion, at the glycosidic carbon. This opening leads most likely first to the β anomer of 11, which mutarotates under the deamination conditions to the more stable α form which was isolated. The α-benzyloxy group migrates from an axial position to a more preferable equatorial position. These results are in agreement with the findings of Cherest et al.[20] A participation by the ring-oxygen free electron pairs can be excluded, in this case, since these orbitals are not in the proper position for backside displacement of diazonium at C-2.

The α-keto sugar 8 was further treated with acetic acid and water to give a de-O-benzylidenated compound, 9. The same method was applied to de-O-benzylidenate the 2-O-benzyl compound 11. The resulting compound (**12**) showed decreased optical rotation values after 24 h, which indicated that the solid compound was an α anomer. The IR spectrum was found to be identical with that of an authentic sample sent by A. Klemer of the University of Muenster, West Germany.[28]

Very similar results were obtained for the nitrous acid deamination of benzyl 2-amino-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (**10**). TLC showed three major components, instead of the two found for the manno analogue 7; two of these proved identical with the compounds 8 and 11 isolated before which were formed here in yields of 30 and 11%, respectively.

The third component could not be characterized or crystallized.

The explanation for the products derived from the deamination of **10** is not obvious. In the diazonium ion (**10a**, as shown in Figure 4), the C–N bond at C-2 is equatorial, and only ring bonds are coplanar with it. Consequently, one would expect ring contraction reactions for this compound. The expected 2,5-anhydro-D-mannose derivatives were indeed found by Akiya and Osawa,[25] as products of the deamination of the methyl glycoside analogous to **10**. The formation of the keto sugar 8 and the 2-O-benzylglucose derivative 11 can be explained by internal trans openings of a bicyclic oxonium ion (**10b**)

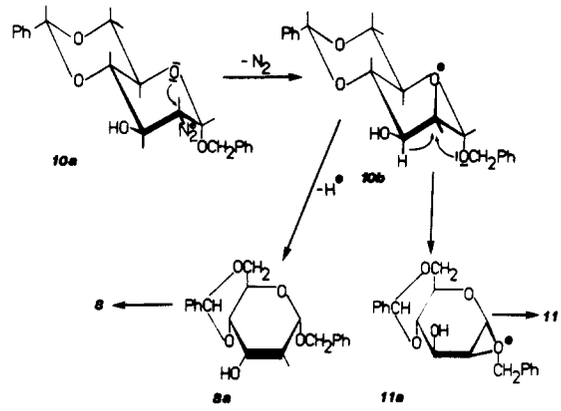

Figure 4. Nitrous acid deamination of benzyl 2-amino-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (**10**) via bicyclic oxonium ion intermediate **10b** gave products 8 and 11.

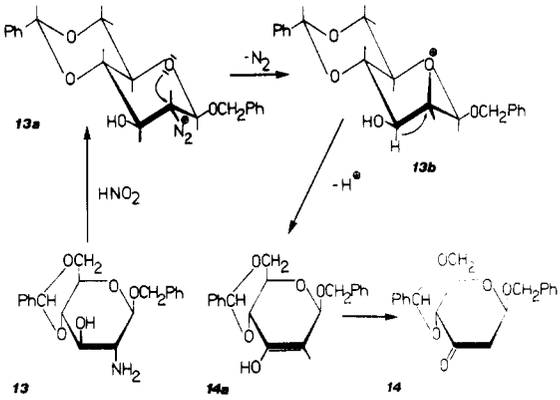

Figure 5. Nitrous acid deamination of benzyl 2-amino-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (**13**) via bicyclic oxonium ion intermediate **13b** gave keto sugar **14**.

resulting from a coplanar bond arrangement preceding the N_2 ejection. Starting from **10b**, the axial proton on C-3 could be expelled by trans elimination leading to the enol **8a**, the precursor of the keto sugar 8. Or, the axial benzyloxy group at C-1 could participate in the oxonium ion collapse, leading to the epoxonium species **11a**, the precursor for the 2-O-benzylglucose derivative 11. The 2,5-anhydromannose derivative found by Akiya and Osawa[25] can be thought to arise from the intermediate bicyclic oxonium ion by cleavage of the bond between C-1 and the ring oxygen. A search of recent literature revealed that bicyclic oxonium ions have been postulated in the deamination of 4-amino-4-deoxy sugars, first by Ng Ying Kin et al. in 1971[29] and then by Brimacombe et al. in 1972.[30,31] Ng Ying Kin et al.[29] postulated a bicyclic oxonium ion intermediate for the deamination of 2-amino-1,5-anhydro-2-deoxy-D-glucitol. Alternatively, one might invoke nucleophilic attack, with inversion at C-2, by the solvent dioxane, to form intermediate "dioxonium" ions that will then react to give the products (e.g., ref 32). However, it is difficult to see why such dioxonium ion intermediates should exist in the sterically hindered axial position derived by inversion at C-2, from **10** and **13**, but should not exist in the less hindered equatorial position that would arise from the deamination of 7.

(27) Tompkins, T. Masters Thesis, University of the Pacific, Stockton, CA, 1972.
(28) Klemer, A. *Chem. Ber.* **1963**, *96*, 634.
(29) Ng Ying Kin, N. M. K.; Williams, J. M.; Horsington, A. *J. Chem. Soc. C* **1971**, 1578.
(30) Brimacombe, J. S.; Al-Radhi, A. K.; Tucker, L. C. N. *J. Chem. Soc., Perkin Trans 1* **1972**, 315.
(31) Brimacombe, J. S.; Minshall, J.; Tucker, L. C. N. *Carbohydr. Res.* **1974**, *35*, 55.
(32) Weiner, H.; Sneen, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 287.

In the nitrous acid deamination of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**13**), the deamination appears to lead first to the diazonium ion **13a** and subsequently to the bicyclic oxonium ion **13b** as in Figure 5. Since the benzyloxy group is now equatorial, we could expect for this compound the following three final products: first, the keto sugar **14**, arising from its enol form **14a**, that was formed by ejection of the axial proton at C-3; second, the 2,5-anhydromannose derivative formed by cleavage of the bond between ring oxygen and glycosidic carbon; third, a 2-deoxyhexonic acid or its lactone, arising from the ejection of the axial glycosidic proton. TLC showed, in fact, three major spots, but only the keto sugar **14** could be isolated in 11% yield, crystallized, and characterized. The 2-*O*-benzylglucose derivative arising from the α anomer was shown to be absent.

Experimental Section

Melting points were taken in a Thomas-Hoover melting point apparatus, Model 6404H. All melting points reported herein are uncorrected. Optical rotations were measured at the sodium D line with an O. C. Rudolph and Sons Inc. Model 956 polarimeter. Infrared spectra were recorded with a Perkin-Elmer spectrophotometer, Model 337, with the potassium bromide pellet technique with a Wilkes pellet compressor. The homogeneities of all compounds synthesized were determined by thin-layer chromatography using a mixture of two parts of Merck silica gel G with one part of Merck silica GF_{254}, the plates being activated by heating at 120 °C for 2 h. The plates were developed with chloroform containing lesser amounts of ethanol, methanol, or acetone. Different solvent systems were used for developing different compounds as indicated in the following separate procedures. The compounds were detected by extinction of the ultraviolet fluorescence of a zinc–silica indicator and also by subsequent spraying with sulfuric acid (10–15%)–methanol and heating for about 15 min at 120 °C. The preparative TLC separations were done on silica gels from Chemie–Erzeugnisse und Adsorptionstechnik AG, Schweiz, on 0.75-mm layers. Elutions of silica gel fractions were done with the solvents indicated in the individual procedures in vessels immersed in an ultrasonic bath. The microanalyses were performed by Beller Mikroanalytisches Laboratorium. A buffer of pH 3.5 was made up for the deamination reactions by dissolving citric acid (12.5 g) and sodium hydroxide (2.0 g) in water (50 mL).

Benzyl 2,3-Anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (2). Procedure A. A solution of benzyl 4,6-*O*-benzylidene-2,3-bis(*O*-methanesulfonyl)-α-D-glucopyranoside (**1**; 30.0 g, 0.06 mol) and sodium methoxide (9.72 g, 0.18 mol) in absolute dioxane (360 mL) and methanol (50 mL) was stirred at 5 °C for 5 h and at room temperature for 6 days. The precipitate was filtered out, and the filtrate was evaporated to dryness in vacuo at room temperature to give a residue. The residue and the precipitate were shaken with water for 5 h. The solids were filtered out and recrystallized from absolute ethanol to give **2** (16.5 g, 81%, mp 189 °C) with an IR spectrum identical with that of the compound prepared by Chiu[26] (lit.[26] mp 180–182 °C). The mother liquor of this recrystallization was used for the isolation of **3**.

Procedure B. Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (**5**; 0.34 g, 1.0 mmol) dissolved in dioxane (12 mL) was mixed with a solution of citrate buffer (8 mL) and sodium nitrite (0.9 g, 13 mmol). The mixture was stirred overnight at room temperature. Saturated sodium bicarbonate solution was added to bring the pH to 7. The precipitate was filtered out and washed with water to give 0.3 g of crude product with only one major component by TLC analysis. Recrystallization from absolute ethanol gave **2**: 0.22 g (65%); mp 191–192 °C; $[\alpha]_D^{23}$ +104° (*c* 1, pyridine); IR spectrum identical with the one obtained from the product under procedure A [lit.[26] mp 180–182 °C; $[\alpha]_D^{25}$ +105° (*c* 1, pyridine)].

Procedure C. Benzyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucopyranoside (**4**; 0.16 g, 0.0045 mol) dissolved in dioxane (5 mL) was added to a solution of sodium nitrite (0.3 g, 4.35 mmol) in citrate buffer (2.5 mL). The solution was stirred at room temperature until TLC indicated the disappearance of the starting material **4**. Saturated sodium bicarbonate solution was added to bring the pH to 7. White precipitate (0.05 g) was filtered out and washed with distilled water (10 mL). The filtrate was extracted with dichloromethane (3 × 35 mL). The extracts were evaporated to give a residue (0.09 g). Both the precipitate and the residue showed three major components by TLC analysis with chloroform/benzene/methanol (17:5:2).

The fast-moving component was isolated by preparative TLC in the same solvent system. It was eluted by chloroform and recrystallized from absolute ethanol to give **2** (0.05 g, 30%, mp 192 °C). The IR spectrum was found to be identical with that of the deamination product of **5** in procedure B.

Benzyl 2,3-Anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (3). The mother liquor obtained from the procedure A of the preparation of **2** was evaporated in vacuo to dryness. The solid residue (0.7 g) was dissolved in hot methylcyclohexane, and benzyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**2**) crystallized on cooling and was filtered out. The filtrate was concentrated and was filtered again. The filtrate was further concentrated and was applied to a preparative TLC plate. The fast-running band, in the solvent system carbon tetrachloride/chloroform (1:1), was eluted by $CHCl_3$. The eluate was evaporated to give a residue that was dried in vacuo and was recrystallized from carbon tetrachloride to give **3**: 0.36 g (2%); mp 128–129 °C; $[\alpha]_D^{23}$ +63° (*c* 1, pyridine); IR (KBr) ν_{max} 1258, 830 (epoxide), 751, 732, 696 cm^{-1} (C_6H_5). Anal. Calcd for $C_{20}H_{20}O_5$ (mol wt 340.36): C, 70.57; H, 5.92. Found: C, 70.93; H, 5.52.

Benzyl, 4,6-*O*-Benzylidene-α-D-altropyranoside (6). Benzyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**3**; 0.1 g, 0.0003 mol) was dissolved in methanol (2 mL), and KOH (2.5 g) in H_2O (2.5 mL) was added. The solution was heated in a sealed autoclave at 125 °C for 24 h. A precipitate, formed after addition of water, was centrifuged out and showed three major components by the TLC analysis with $CHCl_3$ as solvent. The slow component was isolated by preparative TLC and eluted with chloroform to give, after evaporation, **6** (0.01 g, 9%; mp 184 °C). Compound **6** and the sample obtained from Chiu[26] behave the same in TLC analysis, and they gave identical IR spectra.

Benzyl 3-Amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucopyranoside (4). Benzyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**2**; 23.0 g, 0.068 mol) was heated with methanol saturated with ammonia (920 mL) and concentrated ammonium hydroxide solution (230 mL) in a 2-L sealed stainless-steel autoclave at 110 °C for 48 h. From the clear solution, methanol was evaporated in vacuo. The precipitate was filtered out, dissolved in tetrahydrofuran, and reprecipitated with diisopropyl ether. Recrystallization from absolute ethanol gave **5**, identical with the compound prepared by Chiu[26] by IR spectrum and melting point.

The filtrate from the reprecipitation (THF/diisopropyl ether) was evaporated. The dry residue was dissolved in boiling water, and the solution was decanted from impurities. Crystals formed on slow cooling and were recrystallized from a small amount of tetrahydrofuran to give **4**: 0.4 g (1.6%); mp 160–163 °C; mixture melting point with **5**, 140–150 °C; $[\alpha]_D^{25}$ +74° (*c* 0.7, pyridine); IR (KBr) ν_{max} 3350, 3300 (NH), 750, 695 cm^{-1} (C_6H_5). The IR spectrum was different from that of **5** in the regions of 1300–1000 and 800–600 cm^{-1}. TLC on silica gel in $CHCl_3/CCl_4$ (1:1) showed **4** to be different from and free of **5**. Anal. Calcd for $C_{20}H_{23}NO_5$ (mol wt 357.4): C, 67.20; H, 6.49; N, 3.92. Found: C, 67.21; H, 6.29; N, 3.81.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-α-D-*erythro*-hexopyrano-3-uloside (8). Procedure A. Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α-D-mannopyranoside (**7**; 1.9 g, 5.3 mmol) dissolved in dioxane (70 mL) was added to a solution of sodium nitrite (2.5 g, 36.2 mmol) in citrate buffer (40 mL). The solution was stirred at room temperature for 18 h. Saturated sodium bicarbonate solution was added to increase the pH to 7. The filtrate was evaporated to dryness in vacuo. The residue was shaken in distilled water (50 mL). White precipitate (1.35 g) was filtered off and washed twice with distilled water (50 mL). The water phase was extracted with dichloromethane (3 × 35 mL). The extracts were evaporated in a rotary evaporator to give a residue (0.1 g).

Both the precipitate and the residue showed two major products by TLC analysis. Isolation of the faster component by preparative TLC with chloroform/benzene/acetone (13:6:1), after elution with

chloroform, gave 8: 0.85 g (45%); mp 164–165 °C; $[\alpha]_D^{26}$ +105° (c 1, pyridine); IR (KBr) ν_{max} 1740 (C=O), 750, 690 cm^{-1} (C_6H_5) [lit.[27] mp 164–165 °C; $[\alpha]_D^{26}$ +106° (c 1, pyridine); IR (KBr) ν_{max} 1740 (C=O), 750, 690 cm^{-1} (C_6H_5)].

Procedure B. Benzyl 2-amino-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (**10**; 0.17 g, 0.5 mmol) dissolved in dioxane (6 mL) was added to a solution of sodium nitrite (0.46 g, 0.7 mmol) in citrate buffer (4 mL). The solution was stirred at room temperature overnight. Saturated potassium bicarbonate solution was added for neutralization. The filtrate was evaporated to dryness in vacuo and the residues were shaken in distilled water (15 mL). White precipitate (0.1 g) was filtered out and washed with distilled water (5 mL). The water phase was extracted three times with dichloromethane (40 mL). The solvent was evaporated in vacuo to give a residue (0.03 g).

Both the precipitate and the residue showed three major components by TLC analysis. Isolation of the second fast component by preparative TLC with chloroform/benzene/acetone (13:6:1), after elution with chloroform and crystallization from methylcyclohexane, gave 8 (0.05 g, 30%; mp 160–163 °C) identical with that of the deamination product of **7** in procedure A above by comparison of IR spectra.

Benzyl 4,6-O-Benzylidene-2-deoxy-β-D-*erythro*-hexopyrano-3-uloside (14). Benzyl 2-amino-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (**13**; 0.36 g, 1.0 mmol), dissolved in dioxane (12 mL), was added to a solution of sodium nitrite (0.9 g, 1.4 mmol) in citrate buffer (8 mL). The solution was stirred at room temperature overnight. Saturated potassium bicarbonate solution was added for neutralization. The filtrate was evaporated to dryness in vacuo. The residues was shaken in distilled water (30 mL). White precipitate (0.14 g) was filtered out and washed with distilled water (20 mL). The water phase was extracted with dichloromethane (3 × 35 mL). The extracts were evaporated in a rotary evaporator to give an oily residue (0.11 g).

Both the precipitate and the residue showed three major components by TLC analysis. Isolation of the fast component by preparative TLC with chloroform/benzene/acetone (13:6:1), after elution with chloroform and crystallization from methylcyclohexane, gave **14**: 0.04 g (11%); mp 183 °C; $[\alpha]_D^{26}$ −74.1° (c 0.54, dichloromethane); IR (KBr) ν_{max} 1740 (C=O), 750, 730, 685 cm^{-1} (C_6H_5). Anal. Calcd for $C_{20}H_{20}O_5$ (mol wt 340.36): C, 70.57; H, 5.92. Found: C, 69.98; H, 5.93.

2-O-Benzyl-4,6-O-benzylidene-α-D-glucopyranose (11). Procedure A. From the TLC separation of 8 (procedure A above), the slow component was eluted with chloroform and recrystallized from chloroform/methylcyclohexane to give **11**: 0.5 g (26%); mp 175 °C; $[\alpha]_D^{24}$ +150° (5 min) and +6° (1 and 4 h) (c 1, pyridine); IR (KBr) ν_{max} 3425 (OH), 750, 700 cm^{-1} (C_6H_5). Anal. Calcd for $C_{20}H_{22}O_6$ (mol wt 358.4): C, 67.02; H, 6.19. Found: C, 67.17; H, 6.24.

Procedure B. From the TLC separation of 8 (procedure B above), the slowest component was eluted with chloroform and recrystallized from chloroform/methylcyclohexane to give **11**: 0.02 g (11%); mp 175 °C; $[\alpha]_D^{24}$ +140° (5 min) and +10° (1 and 4 h). The IR spectrum was identical with that of the product obtained in procedure A.

Benzyl 2-Deoxy-α-D-*erythro*-hexopyrano-3-uloside (9). Benzyl 4,6-O-benzylidene-2-deoxy-α-D-*erythro*-hexopyrano-3-uloside (**8**; 0.17 g, 0.5 mmol) was heated in glacial acetic acid (6.0 mL) and water (1 mL) at 73 °C for 30 min. Water (4 mL) was added, and the solvents were evaporated in vacuo at a bath temperature below 50 °C. More water (4 mL) was added and evaporated in vacuo followed by methanol (4 mL) and toluene (4 mL) with subsequent evaporations until the residue was dried. It was recrystallized from hot methylcyclohexane to give **9**: 0.09 g (71%); mp 82.5–83.5 °C; $[\alpha]_D^{24}$ +128.5° (c 1, methanol); IR (KBr) ν_{max} 3350, 1280 (OH), 1720 (C=O), 740, 695 cm^{-1} (C_6H_5). Anal. Calcd for $C_{13}H_{16}O_5$ (mol wt 252.29): C, 61.77; H, 6.38. Found: C, 61.60; H, 6.51.

2-O-Benzyl-α-D-glucose (12). 2-O-Benzyl-4,6-O-benzylidene-α,D-glucopyranose (**11**; 0.1 g, 0.27 mmol) was dissolved in glacial acetic (4 mL), and water (2 mL) was added. The solution was heated to 76 °C for 2 h. Water (4 mL) was then added, and the solvents were evaporated in vacuo at a bath temperature below 50 °C. More water (4 mL) was added and evaporated in vacuo, followed by methanol (4 mL) and toluene (4 mL) with subsequent evaporations until the residue was dried. The compound was recrystallized from hot methylcyclohexane to give **12**: 0.07 g (93%); mp 176–177 °C; $[\alpha]_D^{26}$ +61° (5 min) and +45° (24 h) (c 1, methanol); IR (KBr) ν_{max} 3475, 1275 (OH), 750, 700 cm^{-1} (C_6H_5) [lit.[28] mp 176–177 °C; $[\alpha]_D^{23}$ +56° (15 min) and +47° (24 h) (c 1, methanol)]. The IR spectrum was identical with that of the authentic sample obtained from Klemer.[28]

Registry No. 1, 72869-07-9; 2, 35905-39-6; 3, 35905-31-8; 4, 72869-08-0; 5, 72869-09-1; 6, 72869-10-4; 7, 38191-76-3; 8, 72869-11-5; 9, 72869-12-6; 10, 13347-83-6; 11, 72869-13-7; 12, 58719-77-0; 13, 13347-79-0; 14, 72869-14-8.