The AutoAnalyzer was calibrated with equal molar solutions of D-glucose or sodium D-glucuronate monohydrate and the appropriate phenol. The calibration for the instrument was established with three to four analyses at four to six concentration levels.

Calculation of Rate Constants.—From a knowledge of the concentration of the products and the initial glycoside concentration, the fraction of the glycoside unreacted was calculated. It was assumed that each mole of glycoside hydrolyzed produced 1 mole of D-glucuronic acid or D-glucose. Plots of the natural logarithm of the fraction of glycoside unreacted *vs.* time were made. The first-order rate constants were calculated by least-squares, straight-line fits with estimated standard deviations about ±1–2%. Duplicate rate-constant determinations agreed within ±2.0%.

Acknowledgment.—Sincere appreciation is expressed to Dr. J. W. Green for a sample of phenyl β-D-glucoside, and to E. E. Dickey for his many suggestions.

Synthetic Nucleosides. LVIII.[1,2] Studies on the Synthesis of *cis*-2,3-Diamino Sugars. I. The Nitroguanidine Neighboring Group

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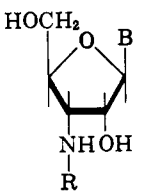
1-(2-Mesyloxyethyl)-3-nitroguanidine (XIV) rapidly cyclized in pyridine at 40° to the imidazoline (XV), a precursor to the ethylenediamine system formed by a neighboring group reaction. In contrast, the sugar pyranoside, methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-mesyl-3-(3-nitroguanidino)-α,D-altropyranoside (XXII), failed to cyclize even in boiling pyridine. Anionic cyclization of XXII with a strong base led to the thermodynamically unstable tricyclic imino sugar derivative (XXIV) rather than the expected and more stable tricyclic imidazoline (XXI). Even methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-2-*O*-mesyl-α,D-altropyranoside (XXVI), when treated with a strong base, was converted to the imino sugar (XXV) *via* an anion; this result contrasts to the cyclization of XXVI to an oxazoline (VI) in the presence of sodium acetate.

The antibiotic, puromycin (I), was the first example of an inhibitor derived from a nucleoside by replacement of a hydroxyl group by an amino function.[3,4] The corresponding aminonucleoside (II) also had interesting biological properties.[4,5] Among the analogs of puromycin synthesized for biological evaluation was the adenine analog (III),[6] which was subsequently



IV

I, B = 6-dimethylamino-9-purinyl
R = *p*-methoxy-L-phenylalanyl
II, B = 6-dimethylamino-9-purinyl
R = H
III, B = 6-amino-9-purinyl
R = H

isolated from *Helminthosporium* sp., and *Cordyceps militaris*.[7] The corresponding 2,3-diamino-2,3-dideoxy-D-ribonucleosides (IV) represented a logical extension of structural modification of II that would be worthy of biological evaluation if these could be synthesized; in addition, no synthesis of a *cis*-2,3-diamino sugar had been reported,[8] and the projected synthetic schemes represented an unexplored area of neighboring group reactions.

The use of a neighboring group reaction for inversion of the configuration of an amino sugar from a *trans* system (V) to *cis* (VI) was introduced into the carbohydrate field by Baker and Schaub[9,10] and fruitfully has been extended by Jeanloz, *et al.*,[11] and others (Scheme I). That the same principle[12] could be used for the introduction of an amino function (VIII)[13] or a sulfur function (X)[14,15] into the pyranose ring of a glycoside subsequently was shown. A logical extension for synthesis of the *cis*-diamino system (XII) would be the use of the appropriate nitrogen derivative of amino sugar XI. In this paper is presented our investigations with the nitroguanidine neighboring group; in the accompanying papers are presented studies with the urea, guanidine, and thiourea neighboring groups.

(1) This work was generously supported by Grant CY-5845 of the National Cancer Institute, U. S. Public Health Service.

(2) For the previous paper of this series, see B. R. Baker and H. S. Sachdev, *J. Org. Chem.*, **28**, 2135 (1963).

(3) For a review of the studies leading to the synthesis of puromycin and some of its analogs, see B. R. Baker, "The Chemistry and Biology of Purines," G. E. W. Wolstenholme and C. M. O'Conner, Ed., J. and A. Churchill Ltd., London, 1957, pp. 120–133.

(4) For a review of the biological properties of puromycin and its analogs, see B. H. Hutchings, *ibid.*, pp. 177–191; M. B. Yarmolinsky and G. L. de la Haba, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1721 (1959), have shown that puromycin can inhibit protein synthesis at the s-RNA level.

(5) B. R. Baker, J. P. Joseph, and J. H. Williams, *J. Am. Chem. Soc.*, **76**, 2838 (1954); **77**, 1 (1955).

(6) B. R. Baker, R. E. Schaub, and H. M. Kissman, *ibid.*, **77**, 5911 (1955); E. J. Reist and B. R. Baker, *J. Org. Chem.*, **23**, 1083 (1958).

(7) (a) N. N. Gerber and H. L. Lechevalier, *ibid.*, **27**, 1731 (1962); (b) A. J. Guarino and N. M. Kredich, *Biochem. Biophys. Acta*, **68**, 317 (1963).

(8) R. D. Guthrie and D. Murphy, *Chem. Ind.* (*London*), 1473 (1962), recently have synthesized methyl 2,3-diamino-2,3-dideoxy-α,D-mannopyranoside by treatment of methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-tosyl-α,D-altropyranoside with sodium azide, followed by reduction. The synthesis of the corresponding alloside from a 3-azido-2-tosyl-D-altropyranoside was unsuccessful (private communication from Dr. Guthrie).

(9) B. R. Baker and R. E. Schaub, *J. Org. Chem.*, **20**, 646 (1954); *J. Am. Chem. Soc.*, **75**, 3864 (1953).

(10) This reaction was based on a similar study in the cyclohexane area by G. E. MacCasland, R. K. Clark, Jr., and H. E. Carter, *ibid.*, **71**, 637 (1949).

(11) R. W. Jeanloz, *ibid.*, **79**, 2591 (1957), and related papers by Jeanloz and co-workers.

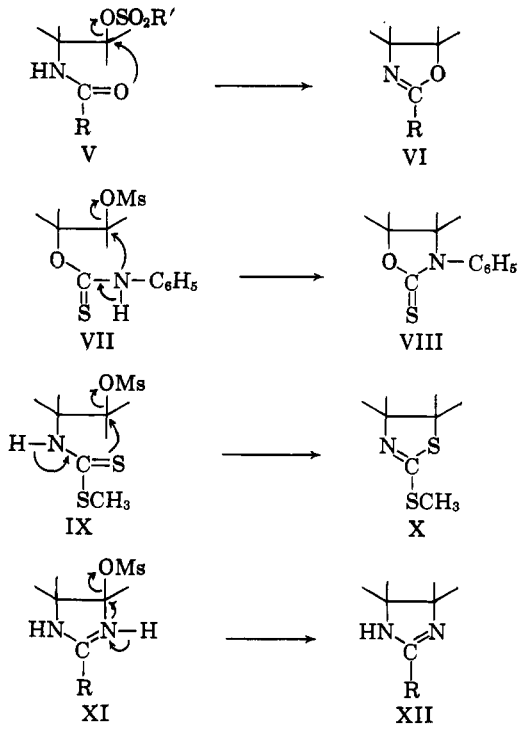
(12) S. Winstein and R. Boschan, *ibid.*, **72**, 4669 (1950), have discussed the probable generality of neighboring group reactions for introduction of other hetero atoms into a chain or ring, but did not carry the study past that reported by MacCasland, *et al.*[10] Later F. L. Scott, R. E. Glick, and S. Winstein, *Experientia*, **13**, 183 (1957), reported results with urea and urethane neighboring groups.

(13) B. R. Baker, K. Hewson, L. Goodman, and A. Benitez, *J. Am. Chem. Soc.*, **80**, 6577 (1958).

(14) L. Goodman and J. E. Christenson, *ibid.*, **83**, 3823 (1961); **82**, 4738 (1960).

(15) W. M. zu Reckendorf and W. A. Bonner, *Chem. Ind.* (London), 429 (1961).

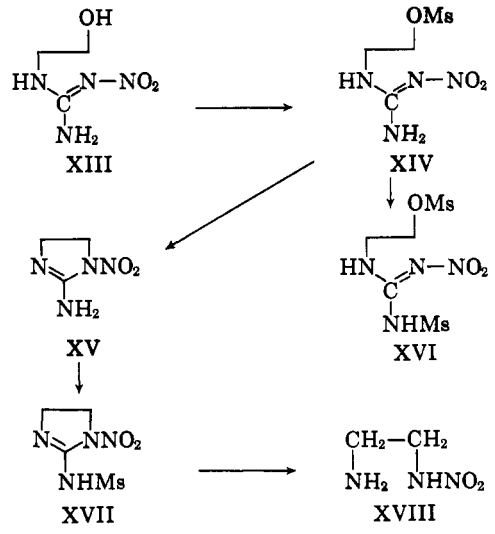
SCHEME I



In a study of 1-substituted 3-nitro-1-nitrosoguanidines as antileukemic agents, Baker, *et al.*,[16] noted that mesylation[17] of 1-(β-hydroxyethyl)-3-nitroguanidine (XIII) led not to the expected *O*-mesyl derivative (XIV), but cyclization and further mesylation, or *vice versa*, to the imidazoline (XVII) occurred[18] (Scheme II). Since the ease of cyclization suggested that the nitroguanidine neighboring group might be of use for synthesis of *cis* diamines in the carbohydrate area, the details of the conversion of XIII to XVII were investigated.

Mesylation of XIII with two equivalents of mesyl chloride in pyridine at 0° gave the mono-*O*-mesyl derivative (XIV) in 65% yield and none of XVI or XVII could be isolated; however, if no precautions were taken to avoid localized heating during the acid chloride addition, then XVII could be isolated in poor yield.[16] When XIV was warmed to 40° in pyridine for 5 min. and then allowed to stand at ambient temperature, cyclization to the methanesulfonate salt of XV occurred in 86% yield. The free base (XV) could be obtained by addition of cold aqueous ammonia to an aqueous solution of the salt; XV was identical with an authentic sample,[18,19] and the authentic sample could be converted to the same methanesulfonate salt by adding methanesulfonic acid to a methanol solution of XV. Treatment of XV, its hydrochloride, or its methanesulfonate salt with methanesulfonyl chloride in pyridine at 0° gave XVII in about 75% yield. Thus, the original formation[16] of XVII from XIII must have

SCHEME II



proceeded *via* XIV and a salt of XV and not XVI as previously proposed.[16] From the studies of McKay,[20] it could be anticipated that XV or XVII could be converted to ethylenediamine by hydrolysis and reductive cleavage; aqueous potassium hydroxide readily cleaved XVII to potassium methanesulfonate (isolated) and 2-aminoethylnitramine (XVIII). The presence of XVIII was determined by paper chromatography in 1-butanol–acetic acid–water (5:3:2) as an ultraviolet absorbing spot (R_f 0.62) that gave a purple ninhydrin color.

Condensation of 1-methyl-3-nitro-1-nitrosoguanidine[20] with the aminoaltroside (XIX)[21] in 70% ethanol at 50° gave the nitroguanidine derivative (XX) in 70% yield. In a pilot run, a lower melting dimorph, m.p. 220°, was isolated; in all subsequent runs, a higher melting dimorph, m.p. 270°, was obtained. The infrared spectrum of the higher melting dimorph in the 6.0–6.8-μ region was similar to that of the model compound, XIII, whereas the lower melting form was quite different in this region; the lower melting form could be converted to the higher melting form on recrystallization from alcohol. The gross difference in the infrared spectra in the 6.0–6.8-μ region indicates that these two compounds may be double bond tautomers. That the nitroguanidyl residue could be split to an amine was shown by basic hydrolysis of XX back to XIX.

Mesylation of XX with either one or two equivalents of mesyl chloride in pyridine at 0 or 25° gave the monomesyl derivative (XXII) in 92% yield as an analytically pure, solid gum suitable for further transformations (Scheme III). Crystallization led to about 40% loss and was considered uneconomical. That cyclization to the methanesulfonate salt of XXI or an isomer (XXIV) had not occurred was demonstrated by the fact that the mesyl group was covalently bound. When refluxed for several hours in pyridine with or without triethylamine, the *O*-mesyl derivative (XXII) was recovered unchanged, whereas long boiling caused decomposition and XXI was not formed; this result

(16) W. A. Skinner, H. F. Gram, M. O. Greene, J. Greenberg, and B. R. Baker, *J. Med. Pharm. Chem.*, **2**, 299 (1960).

(17) The following structural abbreviations are used: Ms, methanesulfonyl; Ac, acetyl; Me, methyl.

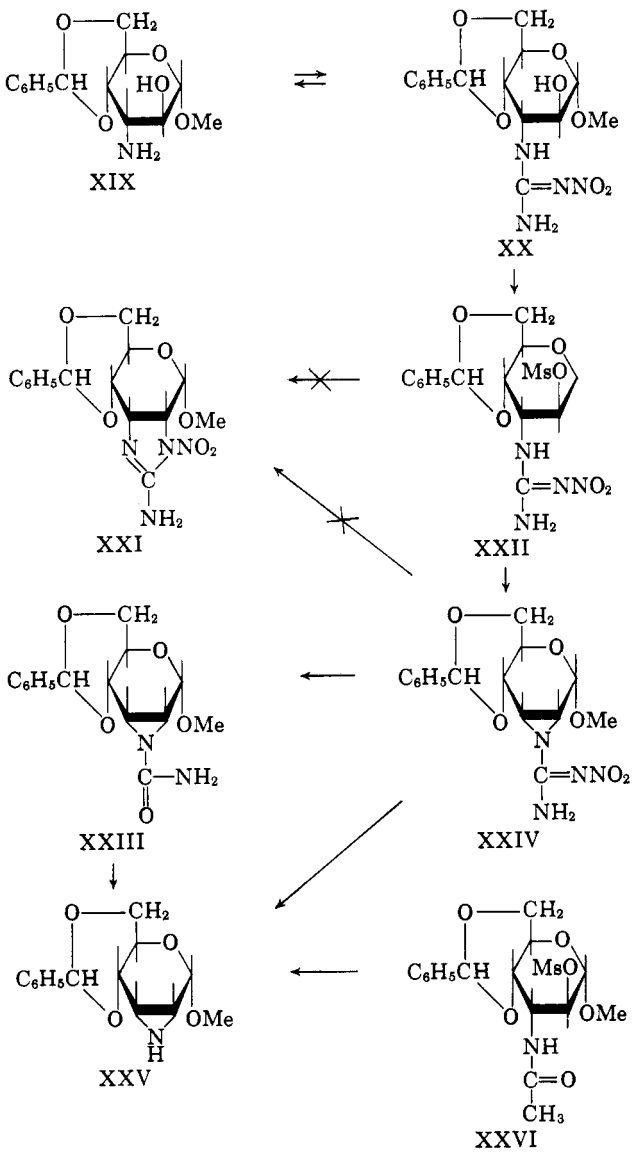
(18) The ready cyclization of 1-(β-chloroethyl)-3-nitroguanidine to the imidazoline (XV) had been observed previously by A. F. McKay and J. E. Milks [*J. Am. Chem. Soc.*, **72**, 1618 (1950)].

(19) If concentrated aqueous ammonia were used for neutralization, ring cleavage occurred to give a mixture of 1-(β-nitraminoethyl)urea and the corresponding guanidine.

(20) A. F. McKay, *Chem. Rev.*, **51**, 301 (1952).

(21) Prepared by the method of W. H. Myers and G. J. Robertson, *J. Am. Chem. Soc.*, **65**, 8 (1943), as modified by B. R. Baker and R. E. Schaub.[9]

SCHEME III

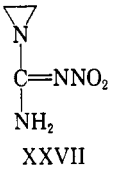


contrasts with the ease of ring closure of the open-chain mesylate (XIV) to XV.

When the mesylate (XXII) was treated with cold ethanolic sodium ethoxide, sodium methanesulfonate rapidly separated. Processing of the reaction mixture afforded 76% yield of a cyclic nitramino derivative, subsequently shown to have the ethylenimine structure XXIV rather than the imidazoline structure XXI. The nitramino group of XXIV was readily hydrolyzed with dilute aqueous base to form XXIII which could be extracted with chloroform. Strong alkaline hydrolysis of XXIV did not give a diamine, as would be expected from XXI, but gave the imino sugar (XXV), identical in properties previously described for XXV prepared by a different route[14]; in fact, treatment of the *O*-mesyl derivative (XXII) with aqueous base gave directly the imino sugar (XXV) in 61% yield, presumably *via* XXIV and XXIII. The ease of formation of an ethylenimino derivative (XXIV) from the mesylate (XXII) is certainly surprising since XXIV has a highly strained tricyclic system which is thermodynamically less stable than the tricyclic imidazoline XXI; however, formation of an imino sugar by anionic attack has been observed previously,[14] and additional examples can be found in the accompanying papers. In fact, even the prototype compound XXVI, first used in a neighboring group reaction on a glycoside to form an oxazoline (VI) with sodium acetate, formed XXV in 75 and 90% yield when treated with methanolic or aqueous base, respectively. A similar observation has recently been noted with the neighboring benzamido group, except that the more stable *N*-benzoyl derivative of XXV was obtained.[22]

Attempts to rearrange the nitro imine (XXIV) to a thermodynamically more stable imidazoline such as XXI or an isomer gave unchanged XXIV below temperatures and times causing decomposition; the more nucleophilic *N*-dithiocarbomethoxy derivatives of XXV have been rearranged to thiazolines.[14]

Since an aziridine was not observed in the model series when XIV was prepared or treated, the aziridine (XXVII) was synthesized from ethylenimine and 1-methyl-3-nitro-1-nitrosoguanidine in 80% yield when the components were reacted at 0° in ethanol.[23] When refluxed in ethanol, this crystalline material was highly unstable and polymerized with or without an equivalent of methanesulfonic acid; XXVII even polymerized on standing open to the air, perhaps catalyzed by



XXVII

carbon dioxide. Evans, *et al.*,[23] have shown recently that XXVII could be ring expanded with *p*-toluenesulfonic acid in ethanol in poor yield, or with cyanogen bromide in benzene. It is, therefore, unlikely that XXVII is an intermediate when XIV is cyclized to the imidazoline (XV), although Evans, *et al.*, did not study ring expansion under basic conditions.

Experimental[24]

1-(2-Mesyloxyethyl)-3-nitroguanidine (XIV).—To a stirred suspension of 6.6 g. (0.045 mole) of XIII[16,20] in 25 ml. of reagent pyridine cooled to 0° was added dropwise a chilled solution of 11 g. (0.096 mole) of methanesulfonyl chloride in 12 ml. of reagent pyridine. Solution was complete in a few minutes. After standing at 0° for 2 hr. protected from moisture, the mixture was poured into 200 ml. of ice-water. The product gradually separated at 0° to yield 6.5 g. (65%) of product with m.p. 130° (resolidifies and remelts about 170° dec.); λ_{max} 2.80, 2.90, 2.98, 3.12 (NH), 6.07 (C=N), 6.18, 6.45 (NH, NO_2), 7.45, and 8.55 μ (sulfonate).

Anal. Calcd. for $C_4H_{10}N_4O_5S$: C, 21.2; H, 4.47; N, 24.8; S, 14.1. Found: C, 21.5; H, 4.46; N, 24.8; S, 14.1.

2-Amino-3-nitro-1-imidazoline (XV) Methanesulfonate. A.—A mixture of 7.3 g. of XIV and 100 ml. of reagent pyridine was warmed to 40° then left overnight at ambient temperature. A white crystalline solid separated (4.5 g.) and was collected and washed with 50 ml. of petroleum ether (b.p. 30–60°). By work-up of the filtrate, an additional 2.3 g. was obtained. Recrystal-

(22) R. D. Guthrie, D. Murphy, D. H. Buss, L. Hough, and A. C. Richardson, *Proc. Chem. Soc.*, 84 (1963).

(23) While this manuscript was in preparation, J. U. Lowe, Jr., T. A. Oda, and R. Evans, *J. Org. Chem.*, **28**, 1496 (1963), reported the preparation of XXVII from ethylenimine and 2-methyl-1-nitro-2-thiopseudourea in 80% yield.

(24) Melting points were taken in capillary tubes in a Mel-Temp block; those below 230° are corrected. Infrared spectra were determined in Nujol mull with a Perkin-Elmer 137B recording spectrophotometer. Rotations were determined in a 1-dm. microtube in *N,N*-dimethylformamide unless otherwise indicated; concentrations are indicated in g./100 ml. as %.

lization from methanol yielded 6.3 g. (86%) of product as needles, m.p. 177–178°; λ_{max} 2.88 (NH), 5.83 (C=NH$^+$), 6.43 (NH, NO_2), 7.45, and 8.61 μ (sulfonate).

Anal. Calcd. for $C_4H_{10}N_4O_5S$: C, 21.2; H, 4.47; N, 24.8; S, 14.1. Found: C, 21.2; H, 4.48; N, 24.8; S, 14.2.

To a solution of 1.00 g. of the methanesulfonate salt in 2 ml. of water was added 2.2 ml. of 3 *N* aqueous ammonia. After 5 min. at 0°, the product was collected and yielded 0.55 g. (70%); it had m.p. 128° that was identical with a sample prepared from 1-(2-chloroethyl)-3-nitroguanidine.[18]

B.—To a solution of 0.55 g. of XV, prepared from 1-(2-chloroethyl)-3-nitroguanidine,[18] in 2.5 ml. of methanol was added 0.3 ml. of methanesulfonic acid. Chilling gave 0.77 g. (81%) of the salt, m.p. 176–177°, that was identical with preparation A.

2-Methanesulfonamido-3-nitro-1-imidazoline (XVII).—To a solution of 400 mg. of 2-amino-3-nitro-1-imidazoline (XV)[8] in 3 ml. of reagent pyridine was added 0.3 ml. of methanesulfonyl chloride dropwise with stirring and ice cooling. After an additional 2 hr. at 0°, the mixture was added to 10 g. of ice, and the product was collected on a filter, yielding 480 mg. (75%) with m.p. 166–167°; a melting point of 167–171° has been recorded[6] for this compound and the reported infrared peaks agreed.

Similarly, 750 mg. of the methanesulfonate salt of XV gave 425 mg. (73%) of XVII, m.p. 167–168°.

When 400 mg. of XVII was refluxed for 10 min. with a solution of 0.35 g. of potassium hydroxide in 10 ml. of water, 100 mg. of pure potassium methanesulfonate was isolated by crystallization from aqueous ethanol. Chromatography of the filtrate on paper with butanol–acetic acid–water (5:3:2) showed an ultraviolet absorbing spot at R_f 0.62 that gave a purple color with ninhydrin; these properties correspond to those expected for XVIII.

1-(Nitroamidino)aziridine (XXVII).—To a magnetically stirred solution of 2 g. of ethylenimine in 5 ml. of ethanol cooled in an ice bath was added 2 g. of 1-methyl-3-nitro-1-nitrosoguanidine in small portions over a period of 1 hr. After standing overnight at 0°, the mixture was filtered and the product was washed with cold ethanol to yield 1.4 g. (80%) with m.p. 115°; λ_{max} 2.91, 3.02 (NH), 6.28 (C=N), and 6.61 μ (NO_2).

The compound gradually polymerized on standing in the solid state or on short heating in ethanol.

Anal. Calcd. for $C_3H_6N_4O_2$: C, 27.7; H, 4.65; N, 43.1. Found: C, 27.9; H, 4.79; N, 43.1.

Methyl 4,6-*O*-Benzylidene-3-deoxy-3-(3-nitroguanidino)-α,D-altropyranoside (XX).—To a swirled suspension of 6.6 g. of XIX[2] in 10 ml. of water and 25 ml. of 95% ethanol at 40–50° was added portionwise 2.9 g. of 1-methyl-3-nitro-1-nitrosoguanidine. The mixture was held at this temperature for an additional hour, then chilled overnight at 0°. The product was collected on a filter and washed with 20 ml. of water to yield 6.0 g. (70%) with m.p. 269–270°; λ_{max} 2.88, 2.99, 3.10 (OH, NH), 6.20, 6.40 (NH, C=N), 6.68 (NO_2), 13.2, and 14.3 μ (C_6H_5—); $[\alpha]^{22}D$ 89 ± 1° (0.64%).

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 49.0; H, 5.45; N, 15.2. Found: C, 49.0; H, 5.65; N, 15.0.

In a pilot run, the yield was 600 mg. (70%) of product, m.p. 219–220°, that had a different infrared spectrum from the higher melting dimorph.

Anal. Found: C, 48.7; H, 5.71; N, 14.9.

Refluxing a suspension of the low melting dimorph in ethanol gave the high melting dimorph.

The nitramidine group of XX could be removed when 250 mg. was refluxed with 25 ml. of 0.2 *N* sodium hydroxide for 1 hr. On spin evaporation *in vacuo* to about 10 ml., 153 mg. of crude XIX separated. Recrystallization from methanol gave white crystals, m.p. 183–184°, that were identical with authentic XIX.

Methyl 4,6-*O*-Benzylidene-3-deoxy-2-*O*-mesyl-3-(3-nitroguanidino)-α,D-altropyranoside (XXII).—To a stirred suspension of 4 g. of XX in 30 ml. of pyridine cooled below 5° in an ice bath was added dropwise 2.6 ml. of mesyl chloride over a period of about 10 min. After being stirred an additional 30 min. in the ice bath, the mixture was allowed to stand about 18 hr. at 3–5° protected from moisture. The mixture was poured into 150 ml. of ice–water and the gummy product was extracted with three 100-ml. portions of chloroform. The combined extracts, washed with three 100-ml. portions of water and dried with magnesium sulfate, were spin evaporated to residue *in vacuo* to yield 4.5 g. (92%) of a glass suitable for further transformations. Crystallization from ethanol required several days and about 60% was recovered as nearly white crystals, m.p. 183–184°; λ_{max} 2.90, 2.95, 3.08 (NH), 6.05 (C=N), 6.34 (NH), 6.47 (NO_2), 7.35, 8.40 (sulfonate), 13.2, and 14.3 μ (C_6H_5—); $[\alpha]_D$ +36 ± 1° (0.49%).

Anal. Calcd. for $C_{16}H_{22}N_4O_9S$: C, 43.1; H, 4.94; N, 12.5; S, 7.17. Found for crude product: C, 43.3; H, 4.88; N, 10.8; S, 6.80. Found for recrystallized material: C, 43.1; H, 4.93; N, 12.7; S, 7.11.

Methyl 4,6-Benzylidene-2,3-dideoxy-N-(nitramidino)-2,3-imino-α-D-allopyranoside (XXIV).—To a solution of 500 mg. of XXII in 10 ml. of absolute ethanol at ambient temperature was added 1.5 ml. of 1 *N* methanolic sodium methoxide. After standing for about 18 hr. in a closed flask, the solution was neutralized with solid carbon dioxide, then spin evaporated *in vacuo;* the residue was extracted with two 20-ml. portions of chloroform. The combined extracts, washed with two 20-ml. portions of water and dried with magnesium sulfate, were spin evaporated *in vacuo*. Crystallization from ethanol gave 300 mg. (76%) of product as white needles, m.p. 232–233°; λ_{max} 2.90, 3.00 (NH), 6.28 (C=N), 6.73 (NO_2), 13.4, and 14.4 μ (C_6H_5—); $[\alpha]^{22}D$ +108 ± 1° (0.97%).

Anal. Calcd. for $C_{15}H_{18}N_4O_9$: C, 51.5; H, 5.20; N, 15.9; S, 0.0. Found: C, 51.7; H, 5.36; N, 15.7; S, 0.0.

If the reaction mixture were processed without carbon dioxide neutralization, some hydrolysis to the corresponding carbonyl derivative (XXIII) occurred, as shown by carbonyl absorption at 5.90 μ.

Methyl-4,6-Benzylidene-2,3-dideoxy-2,3-imino-α,D-allopyranoside (XXV). **A.**—A solution of 70 mg. of XXIV in 5 ml. of 0.2 *N* aqueous sodium hydroxide was refluxed for 1 hr., then extracted with three 10-ml. portions of chloroform. The combined extracts, washed with two 10-ml. portions of water and dried with magnesium sulfate, were evaporated *in vacuo*. Recrystallization from ethyl acetate–petroleum ether gave 51 mg. (95%) of white crystals, m.p. 144–145°; λ_{max} 3.05 (NH), 13.3, and 14.3 μ (monosubstituted phenyl), no bands in the 6-7-μ region; $[\alpha]^{22}D$ 145.5 ± 0.8° (0.99%).

Anal. Calcd. for $C_{14}H_{17}NO_4$: C, 63.8; H, 6.52; N, 5.32; mol. wt., 263. Found: C, 63.7; H, 6.59; N, 5.55; mol. wt., 275.

A melting point of 143–145°, but no optical rotation or molecular weight, has been recorded for this compound prepared by a different route.[14]

B.—A solution of 500 mg. of XXII in 25 ml. of 0.2 *N* aqueous sodium hydroxide was refluxed for 1 hr., then processed as in method A to yield 180 mg. (61%). An additional 50 mg. (total, 78%) was obtained by extracting the basic solution 2 days later. Both fractions had melting points and infrared spectra identical with preparation A.

C.—A solution of 50 mg. of XXVI in 5 ml. of methanol and 0.5 ml. of 1 *N* methanolic sodium methoxide was heated to reflux, then cooled, and neutralized with solid carbon dioxide. Methanol was evaporated *in vacuo* and 10 ml. of water was added to the residue. The solution was extracted with three 15-ml. portions of chloroform, then processed as in A to yield 25 mg. (75%) of product, m.p. 143–144°, that gave an infrared spectrum identical with preparation A.

D.—When water was substituted for methanol in preparation C, 30 mg. (90%) of product, m.p. 143–144°, was obtained that gave an infrared spectrum identical with A.

E.—The *N*-acetyl derivative of XXV gave 85 and 96% yields of XXV, respectively, by methods C and D.

Methyl *N*-Acetyl-4,6-benzylidene-2,3-dideoxy-2,3-imino-α-D-allopyranoside.—To a stirred solution of 320 mg. of XXV in 3 ml. of reagent pyridine cooled in an ice bath was added 2 ml. of acetic anhydride. After standing for about 18 hr. in a stoppered flask at room temperature, the solution was diluted with 15 ml. of water and the product was collected on a filter. Recrystallization from ethanol gave white crystals with m.p. 183–184°; λ_{max} 5.95 (amide C=O), 13.3, and 14.4 μ (monosubstituted phenyl), no NH near 3 μ; $[\alpha]^{22}D$ 155 ± 2°.

Anal. Calcd. for $C_{16}H_{19}NO_5$: C, 63.0; H, 6.28; N, 4.59. Found: C, 63.1; H, 6.39; N, 4.56.

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