0.5 mmole) was added tosyl chloride (0.114 g., 0.6 mmole). The solution was kept at room temperature for 1.25 hr. and was then poured onto crushed ice (25 g.). The aqueous solution was extracted with chloroform (three 10-ml. portions) and the combined chloroform solutions were washed with water (two 5-ml. portions), dried, and concentrated to afford crude **17** as a yellow crystalline solid (0.190 g., 87%). Decolorization of the solid in ethanol gave a pale yellow solid which was triturated with ethyl acetate to give **17** (0.100 g., 46%), m.p. 270–275°. Recrystallization from chloroform–petroleum ether furnished the analytical sample: m.p. 268–270°; λ_{max} 2.90, 3.06, (OH, NH), 7.50, 8.60 (sulfonamide), 13.35, and 13.90 μ (phenyl).

Anal. Calcd. for $C_{21}H_{25}NO_7S$ (435.5): C, 57.92; H, 5.79; N, 3.22; S, 7.36. Found: C, 58.04; H, 5.74; N, 3.40; S, 7.19.

Methyl 4,6-*O*-Benzylidene-3-deoxy-3-*O*-methyl-3-methylamino-*N*-(*p*-tolylsulfonyl)-α-D-glucopyranoside (18).—A solution of **17** (0.040 g.) in *N,N*-dimethylformamide was methylated as described for **16** to give a sirup (0.040 g.). After decolorization in ethanol, concentration afforded a friable glass (0.036 g., 85%), $[\alpha]^{20}D$ +25.2 ± 1.3° (1.06%). Upon drying *in vacuo* the glass crystallized to give, after trituration with ethyl acetate–petroleum ether, **18** as short needles: m.p. 166–167°; λ_{max} 7.51, 8.61 (sulfonamide), 13.14, 13.90, 14.39, and 14.70 μ (phenyl).

Anal. Calcd. for $C_{23}H_{29}NO_7S$: C, 59.60; H, 6.30; N, 3.02; S, 6.92. Found: C, 59.75; H, 6.50; N, 2.85; S, 6.59.

T.l.c. of **18**, R_f 0.68, and of **16**, R_f 0.82, showed them to be clearly isomeric.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2,3-imino-α-D-mannopyranoside (13).—A suspension of methyl 4,6-*O*-benzylidene-2-cyanamido-2-deoxy-*N*-(*p*-tolylsulfonamido)-3-*O*-(*p*-tolylsulfonyl)-α-D-altropyranoside (19)[9] (1.228 g., 2.0 mmoles) in ethanol (12.5 ml.) and 0.4 *N* aqueous sodium hydroxide (12.5 ml.) was heated on the steam bath for 2.25 hr. The solution then was cooled, neutralized with carbon dioxide, and extracted with chloroform (four 15-ml. portions). The combined chloroform solutions were washed with water (three 10-ml. portions), dried, and concentrated to give a crystalline residue (0.623 g.). Dissolution of the residue in refluxing ethyl acetate (7 ml.) followed by slow cooling to room temperature afforded a crystalline product. The mixture was diluted with petroleum ether (10 ml.) and filtered to give fine needles (0.278 g.), m.p. 139–175°. The needles were chromatographed in two runs on silicic acid (20 g. of 60–200 mesh, 1 × 34 cm. column) using chloroform–acetone (4:1, v./v.), followed by acetone, as the eluents. In order of elution, methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside,[24] m.p. 198–200° (0.082 g.), methyl 4,6-*O*-benzylidene-*N*-carbamoyl-2,3-dideoxy-2,3-imino-α-D-mannopyranoside[9] (**20a**), m.p. 203–205° (0.141 g., 23%), and **13**, m.p. 140–142° (0.045 g., 9%), were thereby isolated as crystalline compounds.

Analysis by t.l.c. of the glass (0.330 g.) obtained from the filtrate from the 0.278 g. showed it to be a mixture of **13** and the 2,3-anhydro-D-allopyranoside in an approximate ratio of 20:1, respectively. Crystallization from ethyl acetate–petroleum ether gave **13** (0.250 g., 48%): m.p. 135–137°; λ_{max} 3.00 (NH), 7.20 (CH, sharp), 12.10 (NH), 13.26, and 14.36 μ (phenyl) (lit.[4] m.p. 145–146°).

Conversion of **13** to its highly crystalline *N*-acetyl derivative **20b** was performed by allowing a solution of **13** (0.050 g., 0.19 mmoles) in pyridine (1 ml.) containing acetic anhydride (0.12 ml. to stand 1 hr. at room temperature. Concentration gave a crystalline residue which was twice recrystallized from ethanol to give pure **20b** (0.043 g., 72%): m.p. 209–211°; λ_{max} 5.89 (amide I), 7.80 (amide III), 13.21, and 14.36 μ (phenyl), no absorption at 3.0 (NH) or at 6.3 μ (amide II) (lit. m.p. 205–206°,[4a] 211–212°[4b]).

Refluxing a solution of **19** (0.400 g.) in aqueous 0.2 *N* sodium hydroxide (20 ml.) for 2 hr. gave a sirupy product containing **13** and unhydrolyzed **19**, the latter presumably because of its insolubility in the medium. Further hydrolysis of this mixture for 2 hr. in a refluxing solution of 0.2 *N* sodium with 50% aqueous ethanol as the solvent gave **13**, m.p. 140–141°, in 73% yield.

(24) This anhydro derivative undoubtedly arises from incomplete ammonolysis during the preparation of **8**.[9]

Synthetic Nucleosides. LXVIII. Studies on the Synthesis of *cis*-2,3-Diamino Sugars. VIII. Derivatives of 2,3-Diamino-2,3-dideoxy-D-ribose and 2,3-Dideoxy-2,3-imino-D-ribose[1a,b]

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The *N*-methanesulfonyl derivative (**3**) of methyl 3-amino-3-deoxy-2,5-di-*O*-methanesulfonyl-β-D-arabinofuranoside (**13b**) undergoes cyclization in aqueous sodium hydroxide or with sodium acetate in hot *N,N*-dimethylformamide to give methyl 2,3-dideoxy-2,3-imino-*N*-methanesulfonyl-5-*O*-methanesulfonyl-β-D-ribofuranoside (**4**). The cyclization of methyl 3-deoxy-2,5-di-*O*-methanesulfonyl-3-(3-phenylureido)-β-D-arabinofuranoside (**15b**) was also investigated.

Neighboring group reactions have been of considerable utility in achieving synthesis of *cis*-substituted sugars.[2] The success of these facile reactions suggested that neighboring groups, suitably substituted with a nitrogen function, would lead to a convenient synthesis of *cis*-2,3-diamino sugars.[3a] Earlier papers[1a,3,4] in this series have described the synthesis and reactions of the nitroguanidino, thioureido, ureido, and guanidino derivatives of 2- and 3-amino-D-altrose and 2- and 3-amino-D-glucose. In these studies the synthesis of several *cis*-2,3-diamino derivatives of D-allose and D-mannose[3c,d,4a] has been achieved.[5] In addition, when the nucleopholic neighboring group was *trans*-diaxial to the adjacent sulfonate ester and contained a hydrogen on the secondary nitrogen atom, aziridines were formed in strongly basic media.[1a,3,4a] As a continuation of these studies it was of interest to examine the cyclization reactions of selected derivatives of methyl 3-amino-3-deoxy-β-D-arabinofuranoside. These studies are described in this paper.

(1) (a) For the previous paper in this series, see B. R. Baker and T. L. Hullar, *J. Org. Chem.*, **30**, 4049 (1965). (b) This research was supported in part by Grant CY-5845, National Cancer Institute, U. S. Public Health Service. (c) National Science Foundation Postdoctoral Fellow, 1963–1964.

(2) (a) B. R. Baker and R. E. Schaub, *J. Org. Chem.*, **19**, 646 (1954), and subsequent papers; (b) R. W. Jeanloz and D. Jeanloz, *ibid.*, **26**, 537 (1961), and previous papers.

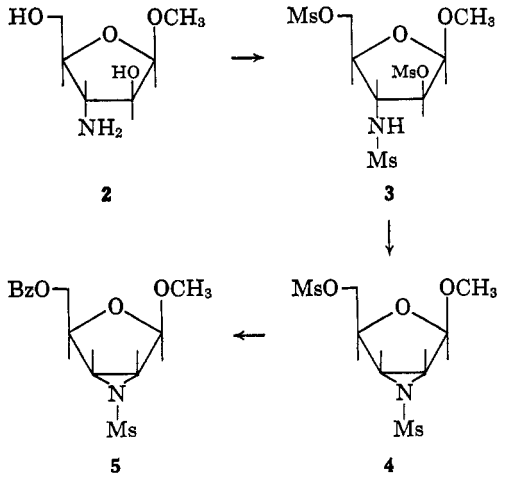
(3) (a) B. R. Baker and T. Neilson, *ibid.*, **29**, 1047 (1964); (b) *ibid.*, **29**, 1051 (1964); (c) *ibid.*, **29**, 1057 (1964); (d) *ibid.*, **29**, 1063 (1964).

(4) (a) B. R. Baker and T. L. Hullar, *ibid.*, **30**, 4038 (1965); (b) B. R. Baker and T. L. Hullar, *ibid.*, **30**, 4045 (1965).

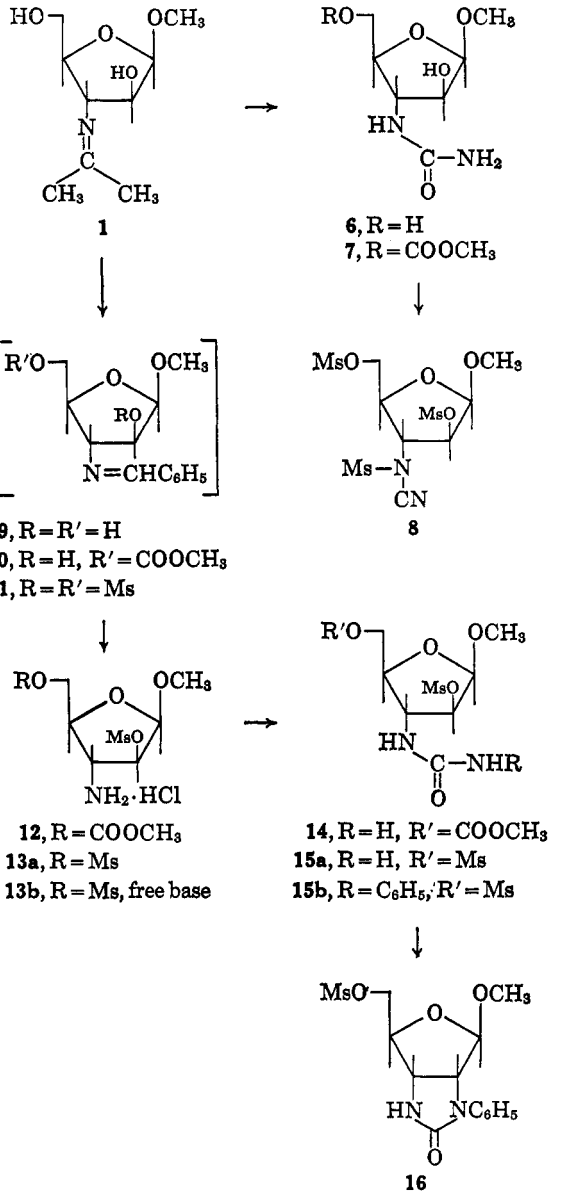
(5) Nucleophilic displacement of sulfonate ion by azide ion followed by reduction of the azide has also furnished *cis*-diamino sugars.[6]

(6) (a) R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, 5288 (1963); (b) W. Meyer zu Reckendorf, *Chem. Ber.*, **97**, 1275 (1964).

SCHEME I



SCHEME II



To study qualitatively the formation of aziridine in a pentofuranose system without the possibility of oxazoline formation, methyl 3-deoxy-3-methanesulfonamido-2,5-di-*O*-methanesulfonyl-β-D-arabinofuranoside (**3**) was synthesized and its cyclization was examined. The action of mesyl chloride on methyl 3-amino-3-deoxy-β-D-arabinofuranoside (**2**)[7] gave **3**[8] in 72% yield (Scheme I). Simply allowing **3** to stand in 1 *N* aqueous alkali at room temperature gave the *N*-mesylaziridine, methyl 2,3-dideoxy-2,3-imino-*N*-methanesulfonyl-5-*O*-methanesulfonyl-β-D-arabinofuranoside (**4**) in 90% yield. To illustrate further the facile cyclization of the methanesulfonamido group in **3** to furnish an aziridine, a solution of **3** with sodium benzoate in *N*,*N*-dimethylformamide[9] at 100° gave methyl 5-*O*-benzoyl-2,3-dideoxy-2,3-imino-*N*-methanesulfonyl-β-D-arabinofuranoside (**5**) in 56% yield.

These results show that aziridine derivatives of D-ribofuranose may be readily obtained. In particular it would appear highly probable that the *N*-acetyl analog of **3** would furnish the corresponding *N*-acetylaziridine[6a,10] which could then be hydrolyzed to the secondary imine.

The synthesis of *cis*-2,3-diamino derivatives of D-ribofuranoside would most conveniently require a derivative, such as **10**, which maintains the suitable *trans* stereochemistry about C-2 and C-3 and contains a readily removed protecting group at C-5. In pursuit of this objective, reaction of methyl 3-amino-3-deoxy-*N*-isopropylidene-β-D-arabinofuranoside (**1**)[7] with aqueous cyanic acid[3b] gave methyl 3-deoxy-3-ureido-β-D-arabinofuranoside (**6**) in 71% yield. However, efforts to prepare the requisite 5-*O*-carbomethoxy derivative **7** in pure form were unsuccessful, apparently owing to acylation at the C-2 hydroxyl occurring at a competitive rate.

The action of excess mesyl chloride[8] on **6** gave methyl 3-cyanamido-3-deoxy-*N*-methanesulfonyl-2,5-di-*O*-methanesulfonyl-β-D-arabinofuranoside (**8**). *N*-Sulfonylation of cyanamides has been observed previously for phenylcyanamide[11] and for methyl 4,6-*O*-benzylidene-2-cyanamido-2-deoxy-α-D-altropyranoside.[4a,12] The addition of benzylamine to **8** can conceivably lead to a guanidine derivative which can cyclize[3d,4a] to a derivative of 2,3-diamino-2,3-dideoxy-D-ribose. However, reaction of **4** with benzylamine failed to furnish a characterizable product.

In consequence, attention was turned to a second series of reactions (Scheme II). Aqueous hydrolysis of **1**, to form the free amine **2**, followed by successive reaction with benzaldehyde, methyl chloroformate,[13] and mesyl chloride gave a crude crystalline product. Again selective carbomethoxylation in the 5-hydroxyl group was not achieved; elemental and spectral analyses indicated the crude product to be a mixture of **12** and methyl 3-amino-2,5-di-*O*-carbomethoxy-3-deoxy-β-D-arabinofuranoside hydrochloride. Treatment of

(7) B. R. Baker, R. E. Schaub, and J. H. Williams, *J. Am. Chem. Soc.*, **77**, 7 (1955).

(8) Abbreviation used in this paper: Ms = mesyl = methanesulfonyl.

(9) E. J. Reist, L. Goodman, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 5775 (1958).

(10) D. H. Buss, L. Hough, and A. C. Richardson, *J. Chem. Soc.*, 5295 (1963).

(11) F. Kurzer, *ibid.*, 1034 (1949).

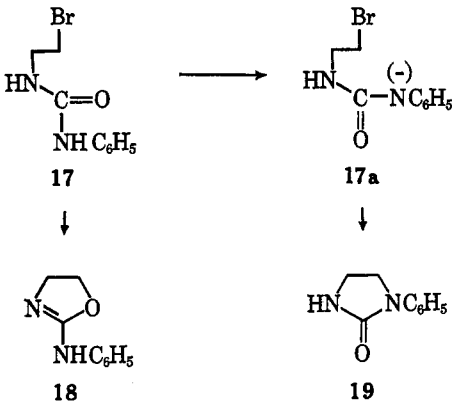
(12) The cyanamides of the methyl 4,6-*O*-benzylidene derivatives of 3-deoxy-α-D-altrose,[3b] 2-deoxy-β-D-glucose,[3b] and 3-deoxy-α-D-glucose,[4b] however, do not readily undergo *N*-sulfonylation. The reason for this anomalous behavior has been discussed previously.[4a]

(13) C. D. Anderson, L. Goodman, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 5247 (1958).

this mixture with aqueous potassium cyanate gave a mixture of ureas which furnished only impure **14**.

Successive treatment (without isolation of the intermediates) of **2** with benzaldehyde, mesyl chloride, and methanolic hydrogen chloride allowed isolation of pure, crystalline methyl 3-amino-3-deoxy-2,5-di-*O*-methanesulfonyl-β-D-arabinofuranoside hydrochloride (**13a**) in 81% over-all yield from **1**. The free base **13a** was also obtained in crystalline form. Reaction of **13a** with aqueous potassium cyanate gave methyl 3-deoxy-2,5-di-*O*-methanesulfonyl-3-ureido-β-D-arabinofuranoside (**15a**) in 91% yield. The action of phenyl isocyanate on **13a** gave methyl 3-deoxy-2,5-di-*O*-methanesulfonyl-3-(3-phenylureido)-β-D-arabinofuranoside (**15b**) in 97% yield.

The ureido function in derivatives of D-altropyranose undergoes neighboring group reactions with an adjacent sulfonate ester to give oxazolines in pyridine solution and aziridines in sodium methoxide solution.[3] On the other hand, previous study of anchimerically assisted displacement reaction of *N*-phenylureas in a simple ethane system (**17**) showed[14] that solvolysis of **17** in a solution with sodium acetate gave the oxazoline **18** whereas treatment of **17** with sodium ethoxide gave the *N*-phenyl imidazolidinone **19**.



Therefore, since **15b** may be considered a derivative of **17**, it was reasonable to expect that **15b**, on treatment with a strong base, should cyclize to furnish the desired cyclic ureide, 1-phenyl-5′-*O*-methanesulfonyl-1′-*O*-methyl-β-D-arabinofurano[3′,2′:4,5]imidazolidinone (**16**).

The action on **15b** of sodium methoxide in refluxing methanol gave a mixture of several products from which a crystalline compound, believed to be **16**, was isolated in 45% yield. Infrared analysis of this product showed it to give absorption at 5.8 μ, indicative of carbonyl absorption for a five-membered cyclic ureide.[15] It was highly improbable that the cyclization product of **15b** was methyl 2,3-dideoxy-2,3-imino-*N*-phenylcarbamoyl-β-D-ribofuranoside since the latter would be expected to have carbonyl absorption nearer to 6.0 μ[3]; the oxazoline resulting from oxygen attack was also unlikely since it would exhibit no absorption below 6.1 μ.

(14) (a) F. L. Scott, R. E. Glick, and S. Winstein, *Experientia*, **13**, 183 (1957). (b) This course of reaction in strongly alkaline media, in contrast to the reaction of monosubstituted ureas in the D-altrose systems,[3c,4a] is likely due to the increased acidity of the hydrogen atom adjacent to the aromatic ring and to resonance stabilization of the derived anion (**13a**).

(15) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day Inc., San Francisco, Calif., 1962.

Experimental Section[16]

Methyl 3-Deoxy-3-methanesulfonamido-2,5-di-*O*-methanesulfonyl-β-D-arabinofuranoside (3).—A solution of methyl 3-amino-3-deoxy-*N*-isopropylidene-β-D-arabinofuranoside (**1**)[7] (0.636 g., 3.18 mmoles) in water (25 ml.) was concentrated to dryness to give **2** as a yellow sirup. To an ice-cooled, stirred solution of the sirupy **2** in pyridine (8.5 ml.) containing triethylamine (0.45 ml., 3.18 mmoles) was added mesyl chloride (1.96 ml., 19.0 mmoles). The solution was kept at 5° for 17 hr. in a stoppered flask, then poured into water (40 ml.) one-half saturated with ammonium sulfate. The aqueous solution was extracted with chloroform (four 20-ml. portions), and the combined chloroform solutions were washed with water (10 ml.), dried, and concentrated to a sirup (0.600 g.). The sirup was decolorized in hot ethanol–ethyl acetate, then crystallized to give white crystals of **3** (0.500 g., 40%), m.p. 140–142°, which were recrystallized from ethanol–petroleum ether, m.p. 142–144°.

The aqueous solution was concentrated to dryness and the residue was suspended in pyridine. After concentration to dryness, the residue was resuspended in pyridine and treated with mesyl chloride as above to give additional **3** (0.410 g., 32%), m.p. 143–144°. Recrystallization from ethanol–ethyl acetate gave pure **3**: m.p. 144–145°; λ_{max} 2.98 (NH), 7.36, 7.50, 7.59, 8.50, and 8.56 μ (sulfonate, sulfonamide).

Anal. Calcd. for $C_9H_{19}NO_{10}S_3$ (397.4): C, 27.20; H, 4.82; N, 3.52; S, 24.20. Found: C, 26.94; H, 4.92; N, 3.38; S, 23.96.

Methyl 2,3-Dideoxy-2,3-imino-*N*-methanesulfonyl-5-*O*-methanesulfonyl-β-D-arabinofuranoside (4).—A solution of **3** (0.100 g.) in 1 *N* sodium hydroxide was kept at room temperature for 3 days and was then neutralized with carbon dioxide. The solution was extracted with three 5-ml. portions of chloroform, and the combined chloroform solutions were washed with water (two 5-ml. portions), dried, and concentrated to a sirup. Upon standing for 1 month, the sirup crystallized to give **4** (0.068 g., 90%), m.p. 120–121°. Recrystallization of crude **4** from ethyl acetate gave pure **4**: m.p. 125–126°; λ_{max} 7.50, 7.55, 7.61, 8.56, and 8.69 μ (sulfonate, sulfonamide), no absorption at 3.0 μ (NH).

Anal. Calcd. for $C_8H_{15}NO_7S$ (301.3): C, 31.89; H, 5.02; N, 4.65; S, 21.28. Found: C, 31.96; H, 5.15; N, 4.47; S, 21.05.

Methyl 5-*O*-Benzoyl-2,3-dideoxy-2,3-imino-*N*-methanesulfonyl-β-D-arabinofuranoside (5).—A stirred mixture of **3** (0.100 g., 0.25 mmole) and sodium benzoate (0.110 g., 0.75 mmole) in *N*,*N*-dimethylformamide (4 ml.) was heated at 90–100° for 9 hr., cooled, then poured into water (10 ml.). The aqueous solution was extracted with chloroform (three 8-ml. portions) and the combined chloroform solutions were washed with water (two 8-ml. portions), dried, and concentrated to a sirup (0.104 g.). Benzoic acid was removed by sublimation *in vacuo*, and the remaining sirup (0.083 g.) was partially crystallized to give a fine needles of **5** (0.046 g., 56%). Recrystallization from ethyl acetate gave pure **5** (0.027 g.): m.p. 134–135°; λ_{max} 5.80 (C=O) 7.59, and 8.73 μ (sulfonyl), no absorption near 3.0 μ (NH).

Anal. Calcd. for $C_{14}H_{17}NO_6S$ (327.4): C, 51.37; H, 5.23; N, 4.28; S, 9.79. Found: C, 51.64; H, 5.24; N, 4.47; S, 9.69.

The mother liquor from the sirup contained predominantly one component (0.037 g., 33%), which was purified by preparative t.l.c.; λ_{max} 3.06 (NH), 5.82, 5.90 (C=O), 7.60, and 8.70 μ (sulfonamide). The data suggested the major component to be a product in which the aziridine ring of **5** has been opened by benzoate ion. The minor product (0.006 g.) in the mother liquor was identified as **4**.

Methyl 3-Deoxy-3-ureido-β-D-arabinofuranoside (6).—To a solution of **1** (0.306 g., 1.50 mmoles) in 95% ethanol (5.7 ml.)

(16) Melting points were taken with a Fisher-Johns melting block and those below 230° are corrected. Infrared spectra were determined in KBr disks, unless otherwise indicated, with a Perkin-Elmer Model 137B spectrophotometer. Petroleum ether used throughout was a fraction of b.p. 30–60°. Thin layer chromatography (t.l.c.) was done with silica gel G using chloroform–acetone (4:1 by volume) as the solvent system; the compounds were detected by exposing the plates to iodine vapor, and the relative proportions of the components were estimated visually. Chloroform extracts were dried over anhydrous magnesium sulfate. All solutions were concentrated by spin evaporation at 60–70° at reduced pressure (aspirator) unless otherwise indicated. Whenever pyridine was employed in a reaction, the residual pyridine in the chloroform extract was always removed by repeated spin evaporation of toluene until the odor of pyridine was absent.

at room temperature was added an aqueous solution of potassium cyanate (0.180 g., 2.22 mmoles) followed by acetic acid (0.11 ml., 2.00 mmoles). The solution was kept at room temperature for 0.5 hr., then refluxed for 1.25 hr., and finally concentrated to dryness *in vacuo*. The residue was dissolved in hot 95% ethanol, and the solution was filtered and kept at 5° overnight. Filtration furnished crystalline **6** (0.220 g., 71%), m.p. 190–195°, which was suitable for further transformations. Concentration of the mother liquors furnished less pure **2** (0.075 g., 24%), m.p. 180–190°. Recrystallization from 95% ethanol gave **2** as needles: m.p. 206–208°; λ_{max} 2.90, 3.00, 3.05 (OH, NH), 6.05 (amide C=O), 6.25, 6.50 (amide NH), and 8.90 μ (C–O–C).

Anal. Calcd. for $C_7H_{14}N_2O_5$ (206.2): C, 40.77; H, 6.85; N, 13.58. Found: C, 40.91; H, 7.01; N, 13.51.

Methyl 3-Cyanamido-3-deoxy-*N*-methanesulfonyl-2,5-di-*O*-methanesulfonyl-β-D-arabinofuranoside (8).—To an ice-cooled, stirred suspension of **6** (0.103 g., 0.50 mmole) in pyridine (1.4 ml.) was added mesyl chloride (0.26 ml., 3.43 mmoles) dropwise during 45 min. After standing 5 hr. at 5° in a stoppered flask, the mixture was poured into ice (20 g.), sodium bicarbonate (2 g.), and pyridine (10 ml.). The aqueous mixture was extracted with seven 15-ml. portions of chloroform and the combined chloroform solutions were washed with two 15-ml. portions of water, dried, and concentrated to a solid residue (0.199 g.). The yellow crystals were washed with chloroform (five 1-ml. portions) until the crystals were colorless. Recrystallization from chloroform–petroleum ether gave pure **8** (0.172 g., 81%): m.p. 147–149°; λ_{max} 4.46 (C≡N), 7.27, 8.45 (sulfonate), 7.42, and 8.62 μ (sulfonamide).

Anal. Calcd. for $C_{10}H_{18}N_2O_{10}S_3$ (422.4): C, 28.43; H, 4.29; N, 6.63; S, 22.77. Found: C, 28.06; H, 4.25; N, 6.64; S, 22.28.

Reaction of **6** (0.203 g., 1.00 mmole) with mesyl chloride (0.252 ml., 3.3 mmoles) in pyridine (2.8 ml.) at 5° for 27 hr. gave a mixture of **8** and partially mesylated **8** as shown by thin layer chromatography. The infrared spectrum showed hydroxyl absorption at 2.8 μ.

Reaction of **6** (0.440 g., 2.15 mmoles) with mesyl chloride (0.71 ml., 9.45 mmoles) in pyridine (6.1 ml.) at 5° for 36 hr. gave crystalline **8** in 64% yield.

Methyl 3-Amino-3-deoxy-2,5-di-*O*-methanesulfonyl-β-D-arabinofuranoside (13b) and Hydrochloride (13a).—A solution of **1** (2.00 g., 10 mmoles) in water (50 ml.) was concentrated to dryness *in vacuo* to remove the isopropylidene group. A solution of the resulting sirup in ethanol (25 ml.) containing benzaldehyde (1.4 ml., 14 mmoles) was refluxed for 2 hr., concentrated to dryness, and then reconcentrated from a solution of toluene (10 ml.). To an ice-cooled, stirred solution of the sirup in pyridine (20 ml.) was added dropwise 2.2 ml. (29 mmoles) of mesyl chloride. After 5 days at 5° in a stoppered flask the mixture was poured into ice-cold aqueous sodium bicarbonate (50 ml.). The aqueous solution was extracted with chloroform (three 20-ml. portions), then the combined chloroform solutions were washed with water (two 10-ml. portions), dried, and concentrated to a sirup (4.3 g.). A solution of the sirup in methanol saturated with hydrogen chloride was kept at 5° for 3.5 hr. and was then evaporated to dryness. Repeated concentration of the sirup from methanol (two 10-ml. portions) followed by trituration with methanol–petroleum ether gave crude **13a** (3.45 g., 97%). The dark crystals were triturated with chloroform to remove the amber color, and the remaining solid was recrystallized from ethanol to give **13a** (2.89 g., 81%), m.p. 160–166°. The analytical sample was obtained by recrystallization from ethanol–petroleum ether: m.p. 171–174; λ_{max} 3.0–4.0, 6.3 (NH^+), 7.45, 7.55, and 8.55 μ (sulfonate).

Anal. Calcd. for $C_8H_{18}ClNO_8S_2$ (355.8): C, 27.00; H, 5.10; Cl, 9.96; N, 3.94; S, 18.02. Found: C, 27.15; H, 5.12; Cl, 10.03; N, 3.84; S, 17.90.

An aqueous solution of **13a** (0.100 g.) was made alkaline and then extracted with chloroform. Concentration of the dried chloroform solutions gave **13b** (0.045 g., 50%) which was crystallized twice from ethanol to give the analytical sample: m.p. 96–97°; λ_{max} 2.95 (NH), 6.2 (NH), 7.46, and 8.57 μ (sulfonate).

Anal. Calcd. for $C_8H_{17}NO_8S_2$ (319.3); C, 30.09; H, 5.36; N, 4.39; S, 20.08. Found: C, 30.19; H, 5.21; N, 4.49; S, 20.16.

Methyl 3-Deoxy-2,5-di-*O*-methanesulfonyl-3-ureido-β-D-arabinofuranoside (15a).—To solution of **13a** (0.710 g., 2.0 mmoles) in water (3.5 ml.) at room temperature was added potassium cyanate (0.178 g., 2.2 mmoles). The resulting mixture was allowed to stand for 30 min., kept at 5° for 1.5 hr. to complete the crystallization, and then filtered to furnish **15a** (0.657 g., 91%). m.p. 172–175°. The crystals were dissolved in *N*,*N*-dimethylformamide at room temperature. Dilution of the solution with ethanol–petroleum ether gave short needles of pure **15a**: m.p. 174–176°; λ_{max} 2.83, 2.90, 3.02 (NH), 6.00 (amide C=O), 6.48 (amide NH), 7.42, 7.51, 8.55, and 8.60 μ (sulfonate).

Anal. Calcd. for $C_9H_{18}N_2O_9S_2$ (362.4): C, 29.83; H, 5.01; N, 7.73; S, 17.70. Found: C, 29.90; H, 5.16; N, 7.77; S, 17.90.

Methyl 3-Deoxy-2,5-di-*O*-methanesulfonyl-3-(3-phenylureido)-β-D-arabinofuranoside (15b).—A solution of **13a** (1.00 g., 2.81 mmoles) in methanol containing 1 *N* methanolic sodium methoxide (2.8 ml.) was concentrated to dryness *in vacuo* (bath 30°). The residue was supended in 1,2-dimethoxyethane (10 ml.), and phenyl isocyanate (0.35 ml., 3.2 mmoles) was added. The mixture was stirred 2 hr. at room temperature, water (0.5 ml.) was added, and the solution was concentrated to dryness. The product was dissolved in 20 ml. of acetone, filtered from the insoluble diphenylurea, then concentrated to a residue; **15b** was recrystallized from acetone–petroleum ether, m.p. 150–156° (1.20 g., 97% yield). Recrystallization from the same solvents gave the analytical sample: m.p. 155–157° with softening at 153°; λ_{max} 2.95, 3.02, (NH), 6.01 (C=O), 6.25, 6.65 (C=C, aromatic), 6.40 (NH), 7.50, 8.52, 8.60 (sulfonate), 13.20, 13.45, and 14.50 μ (phenyl).

Anal. Calcd. for $C_{15}H_{22}N_2O_9S_2$ (438.5): C, 41.09; H, 5.06; N, 6.39; S, 14.62. Found: C, 41.16; H, 5.10; N, 6.19; S, 14.69.

1-Phenyl-5′-*O*-methanesulfonyl-1′-*O*-methyl-β-D-arabinofurano[3′,2′:4,5]imidazolidinone (16).—A solution of **15b** (0.438 g., 1 mmole) in methanol (10.4 ml.) containing sodium methoxide (3 mmoles) was kept at room temperature for 1.5 hr. and then refluxed for 0.5 hr. The clear yellow solution was neutralized with solid carbon dioxide, then concentrated to dryness. An aqueous suspension of the residue (10 ml.) was extracted with three 10-ml. portions of chloroform and the combined chloroform solutions were washed with two 10-ml. portions of water, dried, and concentrated to a sirup which was decolorized in ethanol to give a yellow sirup (0.289 g.). Crystallization from ethyl acetate–petroleum ether gave **16** (0.154 g., 45%), m.p. 150–152°. Decolorization followed by recrystallization gave pure **16** (0.110 g.): m.p. 154–157°; λ_{max} 2.91 (NH), 5.80 (C=O, with shoulder at 5.86), 6.24 (aromatic C=C), 6.62 (amide NH), 7.40, 7.50, 8.40, 8.50 (sulfonate), 13.26, and 14.45 μ (phenyl).

Anal. Calcd. for $C_{14}H_{18}N_2O_6S$ (342.4): C, 49.11; H, 5.30; N, 8.18; S, 9.36. Found: C, 48.92; H, 5.29; N, 8.27; S, 9.49.

The course of this reaction was followed by removing aliquots after 30, 45, and 60 min. at reflux. T.l.c. of the aliquots showed the 30-min. reaction time to give the least complex reaction mixture. Even so, at least seven products were present.