Anal. Calcd for $C_9H_{12}FN_3O_5$: C, 41.38; H, 4.63; F, 7.27; N, 10.09. Found: C, 41.53; H, 4.69; F, 7.24; N, 16.08.

1-β-D-Arabinofuranosyl-4-thiocytosine (16).—Nucleoside **15** (0.3 g, 1.2 mmoles) was allowed to react with liquid ammonia (15 ml) for 2 days at room temperature. After removal of the ammonia, a yellow glass was obtained which on trituration with methanol solidified, 0.22 g, mp 175–180° dec with prior darkening. The product was purified by dissolving in 95% methanol and filtering. The methanol was evaporated *in vacuo* until precipitation occurred. Short yellow needles, mp 180–185° dec with effervescence (ammonia evolved), $[\alpha]^{25}D$ +94° (*c*, 0.27, 50% ethanol), were obtained. Paper chromatography (system 5:1:1) of nucleoside **16** showed one spot at R_f 0.49 (nucleoside **15**, R_f 0.72). The ultraviolet properties are found in Table I.

Anal. Calcd for $C_9H_{13}N_3O_4S$: C, 41.70; H, 5.06; N, 16.20; S, 12.80. Found: C, 41.69; H, 5.10; N, 16.08; S, 12.44.

2',3'-O-Isopropylideneisocytidine (12).[14a]—A few milliliters of liquid ammonia were allowed to react with 2',3'-O-isopropylidene-2,5'-anhydrouridine **10**[39] (8 mg) for 18 hr at room temperature. Cubic crystals, mp 203–205° (lit. mp 206–207°), crystallized from ethanol. The ultraviolet absorption properties were the same as that reported.[14a] Paper chromatography (system 5:1:1) of **12** showed one spot at R_f 0.81 (nucleoside **10**, R_f 0.90]. Paper electrophoresis (acetate buffer, 900 v, 40 ma, 1 hr) of **12** showed one ultraviolet-absorbing spot with a cathodic migration of +3.3 cm (nucleoside **10**, +2.2 cm).

Hyrolysis of 1-(2-Halogeno-2-deoxy-β-D-ribofuranosyl)cytosine and -uracil.—The cytosine derivative **6** (X = F) and uracil derivative **1** (X = F or Cl) were refluxed in water (6 ml at equal concentrations (0.012 *N*) with methyl red and bromothymol blue as internal indicators. The pH was kept between 5 and 6, and the liberated acid was measured by the periodic addition of 0.05 *N* sodium carbonate (theoretical uptake 1.34 ml). The color of the solutions of **1** (X = F or Cl, R = H) and **6** (X = F) were maintained at yellow to pale green.

A plot of ln (per cent 2'-halogeno nucleoside remaining) *vs.* time gave a good linear relationship. No attempt was made to determine the actual order of the reactions. The pseudo-first-order rate constants were 4.65×10^{-4}, 1.04×10^{-3}, and 1.35×10^{-3} min^{-1} for **1** (X = F, R = H), **1** (X = Cl, R = H), and **6** (X = F), respectively. The products from the reaction of the uracil derivative **1** (X = F or Cl) were 2,2'-anhydro nucleoside **13** (R = H) and 1-β-D-arabinosyluracil (**20**, trace amount) as determined by paper chromatography (system 5:1:1). The product from the cytosine derivative **6** (X = F) was found to be 1-β-D-arabinosylcytosine (**9**) by electrophoresis (acetate buffer).

Registry No.—**1** (X = F, R = H), 784-71-4; **2** (X = Cl), 10190-39-3; **2** (X = F), 10212-13-2; **3** (X = Cl), 10190-40-6; **3** (X = F), 10212-14-3; **4** (X = Cl), 10212-15-4; **4** (X = F), 10212-16-5; **5** (X = Cl), 10212-17-6; **5** (X = F), 10212-18-7; **6** (X = Cl), 10212-19-8; **6** (X = F), 10212-20-1; **6** (X = H), 7321-01-9; **7**, 10212-22-3; **7** picrate, 10212-23-4; **7** hydrochloride, 10212-24-5; **8** hydrochloride, 10212-25-6; **8** hydrobromide, 10212-26-7; **8** HNO_3, 10212-27-8; **8** $HClO_4$, 10239-69-7; **8** acetate, 10212-28-9; **8** picrate, 10190-41-7; **12**, 5975-05-3; **14** (R = H), 10212-30-3; **14** (R = CH_3), 10212-31-4; **14** (R = F), 10212-32-5; **15**, 10190-42-8; **16**, 10212-33-6; **17a**, 1073-37-6; **17a'**, 10212-35-8; **18**, 156-81-0; 5-methylisocylosine picrate, 10212-37-0.

Acknowledgment.—The authors are indebted to Dr. John F. Codington and Miss Iris Wempen for their helpful discussions.

(39) The authors wish to thank Dr. Brian Otter of this institute for this sample.

Specifically Deuterated, Acetylated Derivatives of 2-Amino-2-deoxy-D-glucose. Nuclear Magnetic Resonance Studies on Migration of Acetyl Groups[1-5]

DEREK HORTON, WILLIAM E. MAST,[6] AND KERSTIN D. PHILIPS

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received December 21, 1966

Each of the acetyl group signals in the nmr spectrum of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (**1**) was identified definitively by synthesis of derivatives **2**, **3**, and **4** that are specifically deuterated in individual acetyl groups. The migration of the *N*-acetyl group during conversion of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl chloride (**7**) into 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose hydrochloride (**9**) was studied by nmr and an effective preparative conversion of **7** into **9** is described. Nmr studies on **9**, its anomer (**6**), and some related derivatives, are described.

In the preceding paper[2] in this series, the signal of the acetamido methyl group in the nmr spectra of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (**1**) and its β-D anomer (**5**) was assigned definitively by synthesis of analogs that were deuterated specifically in the acetamido methyl group. In both instances, for spectra measured in chloroform-*d*, the methyl group signal at highest field (τ 8.09) was that of the acetamido methyl group. The present report describes further specific deuteration experiments that permit definitive assignment of each of the acetyl group signals in the nmr spectrum of **1** in chloroform-*d* and benzene.

The 60-Mcps nmr spectra of anomers **1** and **5**, measured in chloroform-*d*,[7,8] show discrete signals for three of the five acetyl groups (Figure 1); the signals of two of the acetyl groups are not resolved. The anomers show the same pattern of signals, at essentially the same chemical shifts,[9] except that the α-D anomer (**1**) shows the lowest field, acetyl group signal at τ 7.81, and the corresponding signal in the β-D anomer (**5**) is observed at τ 7.89. Since **1** and **5** differ only by the fact

(1) Part IV in the series "Anomeric Equilibria in Derivatives of Amino Sugars." For part III see ref 2.

(2) Previous paper in this series: D. Horton, J. B. Hughes, J. S. Jewell, Kerstin D. Philips, and W. N. Turner, *J. Org. Chem.*, **32**, 1073 (1967).

(3) A preliminary report of part of this work has been given: D. Horton, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 5D.

(4) Supported in part by Grants-in-Aid No. 19187 and 170200 from The Ohio State University Development Fund.

(5) Funds for purchase of the nmr spectrometer were provided by the National Science Foundation, Washington, D. C.

(6) National Science Foundation Undergraduate Research Participant, 1965–1966.

(7) D. Horton, *J. Org. Chem.*, **29**, 1776 (1964).

(8) F. W. Lichtenthaler and H. P. Albrecht, *Ber.*, **99**, 575 (1966).

(9) The chemical shifts vary to a small extent (~±0.02 ppm) according to the concentration of the sample, for a range of concentrations from 1% to that of a saturated solution, but the relative shifts of the acetyl group signals remain essentially constant. Similar shifts with concentration have been noted with other acetylated sugars: F. W. Lichtenthaler, personal communication.

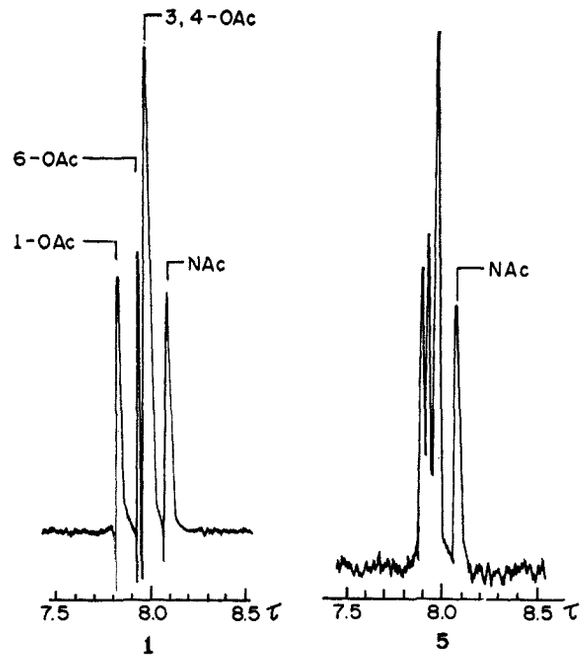
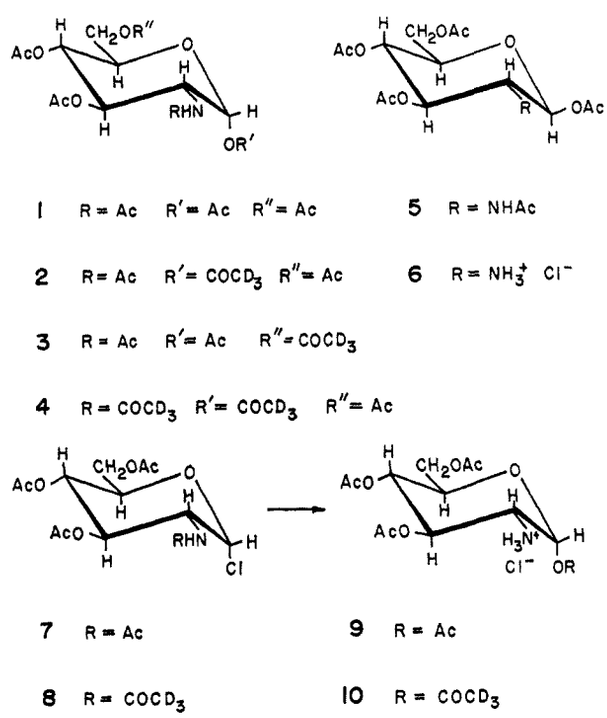


Figure 1.—Signals of the acetyl groups in the 60-Mcps nmr spectra, in chloroform-*d*, of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (**1**) and 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (**5**).

that the 1-acetoxy group is axial in **1** and equatorial in **5**, the signal at τ 7.81 in **1** may be assigned to the 1-acetoxy group. This assignment follows the well-established principle[10,11] that in an anomeric pair of acetylated pyranoses the axial 1-acetoxy group gives a signal at lower field than the equatorial 1-acetoxy group. The spectral ranges for axial acetoxy groups may overlap those where signals of equatorial acetoxy groups are observed, and other substituents may cause specific shielding and deshielding effects,[2] but no exceptions to the general principle[10] have been noted when the two compounds compared are identical except for anomeric configuration.

The signal of the 6-acetoxy group in **1** was definitively identified as the three-proton singlet at τ 7.93, since this signal was absent in the spectrum of 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-trideuterioacetyl-α-D-glucopyranose (**3**). Substance **3** was prepared by detritylation of 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-trityl-α-D-glucopyranose[2,12] with hydrogen bromide in acetic acid, followed by acetylation of the detritylated product with acetic anhydride-d_6 in pyridine. Treatment of the detritylated product, 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose, in pyridine solution, with chlorotriphenylmethane gave quantitative reconversion into the 6-*O*-trityl precursor, indicating that no migration of acetyl groups could have taken place during the steps leading to the 6-*O*-trideuterioacetyl derivative (**3**).

Independent evidence for the assignment of the signal for the 1-*O*-acetyl group in **1** was forthcoming from study of the acetyl group migration[13,14] that takes place when 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride[14,15] (**7**) is treated with water. The reaction leads to formation of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose hydrochloride (**9**), presumably by way of a 1,2-cyclized, oxazolidinium ion intermediate. Attempts to effect the conversion of **7** into **9** under the conditions of Micheel and co-workers[14] (moist chloroform, with or without a trace of acid) gave low yields of **9**. A high-yielding, preparative conversion was effected by refluxing **7** in acetone containing 1 equiv of water, whereupon **9** crystallized directly in pure form from the solution. The nmr spectrum of the product, in deuterium oxide (Figure 2), confirmed that it was the pure α-D anomer (**9**), completely free from the β-D anomer (**6**), indicating that the hydrolysis–migration is completely stereospecific. The spectrum confirmed that four acetyl groups were present; three-proton singlets were observed at τ 7.75 and 7.86, and a six-proton singlet was observed at 7.92. When the hydrolysis–migration reaction was repeated with 3,4,6-tri-*O*-acetyl-2-deoxy-2-trideuterioacetamido-α-D-glucopyranosyl chloride[2] (**8**), the product obtained (**10**) was identical with **9** by melting point and specific rotation, and the two samples gave identical nmr spectra (in deuterium oxide), except that the three-proton singlet at τ 7.75 in the spectrum of compound **9** was absent in the spectrum of **10**. From the nature of



the reaction, the acetyl group at C-1 in **9** must the one that had migrated from the nitrogen atom at C-2 in **7**, and therefore the signal at τ 7.75 in the nmr spectrum (deuterium oxide) of **9** may be assigned definitively to the 1-acetoxy group. Acetylation of **10**, under conditions[2] where acetyl-group migration does not take place, gave 2-acetamido-3 4,6-tri-*O*-acetyl-2-deoxy-1-*O*-trideuterioacetyl-α-D-glucopyranose (**2**), whose nmr spectrum, in chloroform-*d*, was identical with that of the nondeuterated analog (**1**) except that the three-

(10) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).
(11) L. D. Hall, *Advan. Carbohydrate Chem.*, **19**, 51 (1964).
(12) J. M. Anderson and E. Percival, *J. Chem. Soc.*, 814 (1956).
(13) G. Fodor and L. Ötvös, *Ber.*, **89**, 701 (1956).
(14) F. Micheel, F.-P. van de Kamp, and H. Petersen, *ibid.*, **90**, 521 (1957).
(15) D. Horton, *Org. Syn.*, **46**, 1 (1966).

proton singlet at τ 7.81 in the spectrum of **1** was absent in the spectrum of **2**. This establishes that the low-field acetyl group signal in the nmr spectrum of **1** is that of the 1-acetoxy group. Acetylation of **10** with acetic anhydride-d_6 gave a product (**4**) whose nmr spectrum differed from that of **1** by the absence of the signals at τ 7.81 and 8.09, for the 1-*O*-acetyl and *N*-acetyl groups, respectively.

The synthesis of analogs of **1** that are specifically deuterated at the 1-acetoxy group, the 6-acetoxy group, and the acetamido group,[2] permits the complete assignment of acetyl group signals in the nmr spectrum of **1** (Figure 1). In chloroform-*d* the six-proton singlet at τ 7.97 may clearly be assigned to the acetoxy groups at C-3 and C-4.

Spectra of the deuterated derivatives were also measured in acetone-d_6 and in benzene. Assignments of the signals were made as before and the data are listed in Table I. It is particularly noteworthy that,

TABLE I

CHEMICAL SHIFTS OF ACETYL METHYL GROUPS IN 2-ACETAMIDO-1,3,4,6-TETRA-*O*-ACETYL-2-DEOXY-α-D-GLUCOPYRANOSE (**1**), AS ASSIGNED BY SYNTHESIS OF SPECIFICALLY DEUTERATED DERIVATIVES

Solvent	—Chemical shifts[a] (τ) of acetyl group signals, ppm— 1-OAc	NAc	3-OAc	4-OAc	6-OAc
Chloroform-*d*	7.81	8.09	7.97	7.97	7.93
Acetone-d_6	7.90	8.20	*b*	*b*	8.05
Benzene	8.42	8.52	8.32	8.32	8.30

[a] See the Experimental Section for details of measurement. [b] Two three-proton singlets, τ 8.05 and 8.09, assigned to 3-OAc and 4-OAc, but not specifically differentiated.

although the signal of the *N*-acetyl methyl group is still at highest field in these solvents, the signal of the 1-*O*-acetyl group, observed as the lowest field acetyl groups signal in chloroform-*d* and acetone-d_6, is observed in benzene at higher field than all of the other acetoxy group signals.

1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose hydrochloride (**9**) and its β-D anomer[16] (**6**) are very soluble in water, and provide an example of an anomeric pair of sugar acetates whose nmr spectra can readily be observed in deuterium oxide solution (Figure 2). In each case a simple, first-order interpretation of the H-1, H-2, H-3, and H-4 signals is possible because of the fact that the nitrogen atom at C-2 causes the H-2 signal to appear at much higher field than is the case with sugars having an oxygen atom at C-2. Details of the spectral analyses are recorded in the Experimental Section.

Definitive assignment of individual acetyl group signals, in the nmr spectra of acetylated sugars, will permit determination of the position and extent of acetylation, when a sugar is partially acetylated with acetic anhydride, and the acetylation is completed with acetic anhydride-d_6 under conditions that do not permit acetyl migration or exchange. Similar procedures can be used to study selective deacylation and acyl migration. Studies of this type, on **1** and related derivatives, and also studies on fragmentation patterns by mass spectrometry, are in progress.

(16) M. Bergmann and L. Zervas, *Ber.*, **64**, 975 (1931).

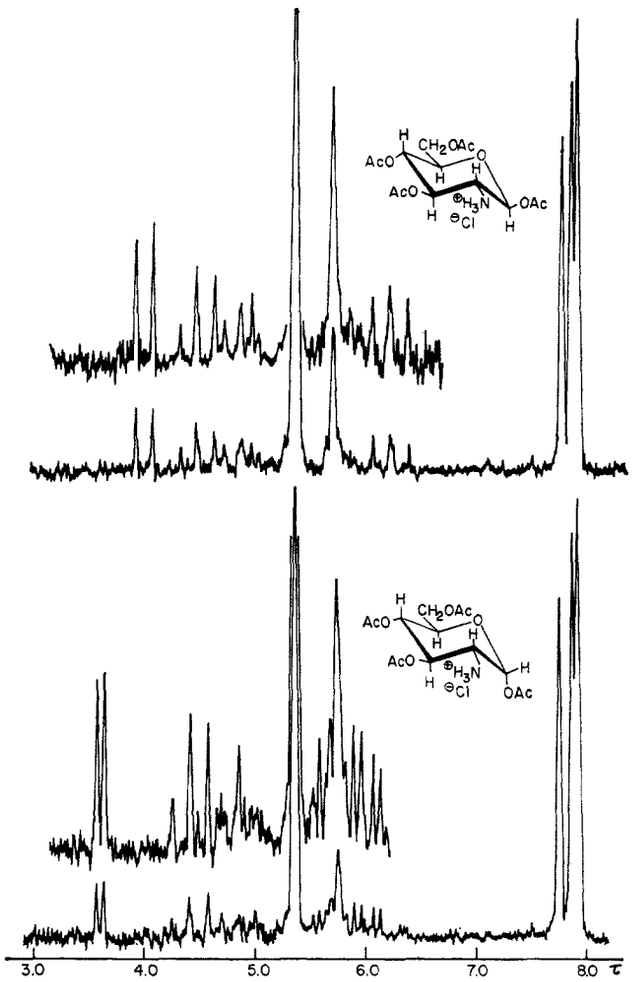


Figure 2.—The 60-Mcps nmr spectra, in deuterium oxide, of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose hydrochloride (**9**) and its β-D anomer (**6**).

Experimental Section[17]

2-Acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose.—A solution of 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-trityl-α-D-glucopyranose[2] (10 g) in acetic acid (32 ml) was cooled to 20°, and a solution of hydrogen bromide in acetic acid that had been saturated at 0° (3.2 ml) was added. The mixture was shaken for 60 sec and then filtered, the filtrate passing directly into 200 ml of a mixture of ice and water. The bromotriphenylmethane that remained on the filter was washed with cold water (200 ml) and the combined filtrate and washings were extracted with 20 200-ml portions of chloroform. The combined extracts were evaporated *in vacuo* without washing, and the product was freed from acetic acid by repeated codistillation with toluene. The product was obtained as a colorless glass: yield 4.1 g (96%); R_f 0.58; λ_{max}^{KBr} 2.98 (OH), 5.70 (OAc), 6.00, 6.45 μ (NHAc), aryl absorptions absent; nmr (chloroform-*d*) τ 4.00 (one-proton doublet, $J_{1,2}$ = 3.5 cps, H-1), 4.14 (one-proton broadened

(17) Melting points were determined with a Thomas–Hoover Unimelt apparatus (Arthur H. Thomas Co., Philadelphia, Pa.). Specific rotations were measured in a 2-dm tube. Infrared spectra were measured with a Perkin-Elmer Infracord infrared spectrometer. Nmr spectra were measured with a Varian A-60 spectrometer, operating at about 40°. Tetramethylsilane (τ 10.00) was used as internal standard with all solvents except deuterium oxide, where sodium 4,4-dimethyl-4-silapentane-1-sulfonate (τ 10.00) was the internal standard. Sample concentrations were approximately 10%. The recorded first-order coupling constants are the measured peak spacings. Elemental analyses were performed by W. N. Rond. X-Ray powder diffraction data give interplanar spacings, A, for Cu Kα radiation. Camera diameter was 114.59 mm. Relative intensities were estimated visually: s, strong; m, moderate; w, weak; v, very. The strongest lines are numbered (1, strongest), double numbers indicate approximately equal intensities. Thin layer chromatography was performed on silica gel G (E. Merck, Darmstadt, Germany) activated at 110°, with 4:1 benzene–methanol as developer and sulfuric acid as indicator.

doublet, $J \sim 9$ cps, shift varies with concentration, disappears on deuteration, NH), 4.75–5.20, 5.50–5.85, 6.28–6.60 (multiplets, six protons, H-2,3,4,5,6,6′), 7.14 (one proton, broad, shift varies with concentration, disappears on deuteration, OH), 7.90, 8.00, 8.14 (three-, six-, three-proton singlets, acetyls).

The product was homogeneous by tlc. A solution of the product (0.521 g) in dry pyridine (2 ml) containing chlorotriphenylmethane (0.418 g, 1 equiv) was shaken for 4 days at room temperature, and the solution was poured into ice and water (50 ml). The product that precipitated was washed with water and dried to yield 810 mg (92%), mp 155–156°, identical with authentic 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-trityl-α-D-glucopyranose[2] by mixture melting point, tlc, comparative infrared and nmr spectra, and by X-ray powder diffraction pattern.

2-Acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-trideuterioacetyl-α-D-glucopyranose (3).—To 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose (1.84 g) were added, in rapid succession, dry pyridine (2 ml) and acetic anhydride-d_6, and the resultant solution was kept for 18 hr at room temperature. The mixture was poured into ice–water (20 ml) and the product was extracted with four 50-ml portions of chloroform. The extract was evaporated and the resultant syrup was codistilled with toluene and then with carbon tetrachloride. Crystallization of the syrup from chloroform–ether gave **3**, yield 1.6 g (76%), mp 138–139°. The product gave an X-ray powder diffraction pattern identical with that of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (**1**); its nmr spectrum (chloroform-*d*) was identical with that of **1** except that the three-proton singlet (τ 7.93) present in the spectrum of **1** was absent in the spectrum of **3**.

Repetition of the experiment with nondeuterated acetic anhydride gave **1** in similar yield, identical with an authentic sample.

1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranose Hydrochloride (9).—A solution of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride[15] (**7**, 25 g) in acetone (500 ml) containing water (1.25 ml, 1 molar equiv) was refluxed gently for 38 hr. The resulting suspension was refrigerated for 1 hr, and the product was filtered and washed with two 50-ml portions of acetone: yield 19–20 g (73–75%); mp 181°; $[\alpha]^{23}D$ +144° (*c* 4.7, water) [lit.[14] mp 180°, $[\alpha]^{20}D$ +130° (*c* 1, water)]; λ_{max}^{KBr} ~3.5, 6.24, 6.35 (NH_3^+), 5.68, 5.74 μ (OAc); nmr (deuterium oxide) τ 3.60 (one-proton doublet, $J_{1,2}$ = 3.7 cps, H-1), 4.42 (one-proton triplet, $J_{2,3}$ = 10.2 cps, H-3), 4.88 (one-proton broadened triplet, $J_{3,4}$ = 9.1 cps, H-4), ~5.75 (three-proton multiplet, H-5,6,6′), 6.02 (one-proton quartet, H-2), 7.75, 7.86, 7.92 (three-, three-, and six-proton singlets, acetyl groups); X-ray powder diffraction 10.34 m, 8.89 s (2), 7.67 w, 6.27 vw, 5.56 m, 5.29 m, 4.93 m, 4.75 vw, 4.51 s (3), 3.90 vs (1), 3.74 w, 3.58 w, 3.38 w, 3.27 m.

Under the same conditions, 3,4,6-tri-*O*-acetyl-2-deoxy-2-trideuterioacetamido-α-D-glucopyranosyl chloride[2] (**8**) was converted into the corresponding 1-*O*-trideuterioacetyl analog (**10**) of **9**. The nmr spectra of **9** and **10** were identical, except that the three-proton singlet observed at τ 7.75 in the spectrum of **9** (deuteriumoxide) was absent in that of **10**.

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-*O*-trideuterioacetyl-α-D-glucopyranose (2).—Substance **10** was acetylated with acetic anhydride in pyridine by the procedure[2] used for preparation of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-trideuterioacetamido-α-D-glucopyranose and substance **3**. The nmr spectrum of the product was identical with that of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (**1**), except that the three-proton singlet at τ 7.81, present in the spectrum of **1** (chloroform-*d*) was absent in the spectrum of **2**.

Repetition of the experiment, with acetic anhydride-d_6, gave 3,4,6-tri-*O*-acetyl-2-deoxy-2-trideuterioacetamido-1-*O*-trideuterioacetyl-α-D-glucopyranose (**4**). The nmr spectrum of **4** was identical with that of **2**, except that the three-proton singlet at τ 8.09 in the spectrum of **2** (chloroform-*d*) was absent in the spectrum of **4**.

1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose Hydrochloride (6).—This product, prepared by the procedure of Bergmann and Zervas,[16] darkened at 210°; $[\alpha]^{21}D$ +29.5 ± 0.5° (*c* 2.8, water) (lit.[16] darkens at 230°, $[\alpha]^{21}D$ +29.7° in water); λ_{max}^{KBr} ~3.6, 6.30 (NH_3^+), 5.70, 5.75 μ (OAc); nmr (deuterium oxide) τ 4.00 (one-proton doublet, $J_{1,2}$ = 8.7 cps, H-1), 4.48 (one-proton triplet, $J_{2,3}$ = 10.0 cps, H-3), 4.88 (one-proton multiplet, $J_{3,4}$ = 9.0 cps, H-4), ~5.70 (three-proton multiplet, H-5,6,6′), 6.23 (one-proton triplet, H-2), 7.77, 7.86, 7.90 (three-, three-, and 6-proton singlets, acetyl groups); X-ray powder diffraction 12.90 w, 8.98 vs (1), 6.01 vw, 5.35 s (2), 4.62 m, 4.24 m, 3.98 vw, 3.76 s (3), 3.57 w, 3.37 w, 3.19 w, 3.02 w, 2.88 w.

Registry No.—2-Acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose, 10034-17-0; **3**, 10034-18-1; **9**, 10034-19-2; **6**, 10034-20-5; **1**, 7784-54-5; **5**, 7772-79-4.

Acknowledgments.—The authors thank Mrs. S. J. Gelb for experimental assistance, and J. S. Jewell, J. B. Hughes, and Dr. J. L. Godman for nmr spectral measurements.

Electrochemical Oxidation of Primary Aliphatic Amines

KAREN K. BARNES AND CHARLES K. MANN

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received November 14, 1966

Ammonia and a series of primary aliphatic amines were oxidized at a platinum electrode in acetonitrile. A dual mechanism is proposed, one sequence of reactions predominating at low potentials, the other at high potentials. The low-potential mechanism involves a one-electron transfer to form a cation radical which decomposes for the most part to a carbonium ion and amidogen radical. At higher potentials, two electrons and a proton are lost to form the iminium salt, which can hydrolyze to aldehyde and ammonia.

We have undertaken an examination of the electrochemical oxidation of primary aliphatic amines as part of a larger study of anodic reactions of nitrogen compounds in which we hope to examine similarities and differences between electrochemical, chemical, and biological oxidations. Previous reports on this work involved anodic oxidation of triethylamine in diemethyl sulfoxide,[1] and oxidation of primary, secondary, and tertiary aliphatic amides.[2] In a survey of aliphatic amine oxidations by cyclic voltammetry,[3] it was noted that while substituent inductive effects could be correlated with voltammetric peak potentials for secondary and tertiary aliphatic amines, this did not apply to primary amines. Further, the voltammetry peaks for primary amines showed characteristically small slopes with the peaks drawn out over an appreciable potential range, as compared with secondary and tertiary amines. No other references to anodic oxidation of primary aliphatic amines appear, although a coulometric titration of amines was described under conditions which would seem, from this work, to involve direct amine oxidation.[4]

(1) R. F. Dapo and C. K. Mann, *Anal. Chem.*, **35**, 677 (1963).

(2) J. F. O'Donnell and C. K. Mann, *J. Electroanal. Chem.*, **13**, 157 (1967).

(3) C. K. Mann, *Anal. Chem.*, **36**, 2424 (1964).

(4) C. A. Streuli, *ibid.*, **28**, 130 (1956).