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5-Amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose[1]

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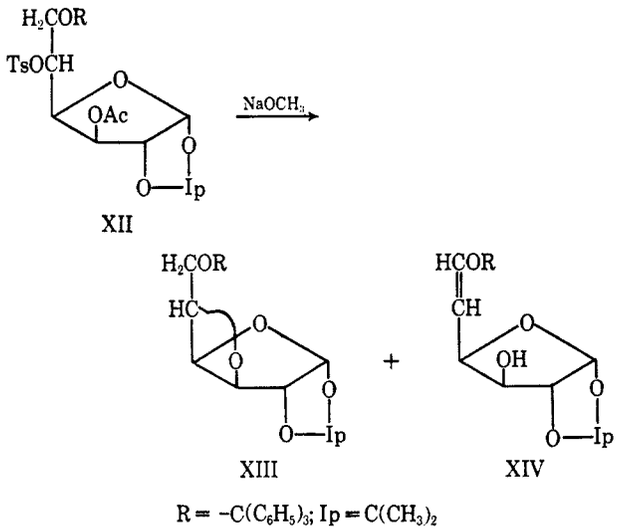
Two convenient routes for the synthesis of 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose are provided by (1) nucleophilic displacement of the *p*-tolylsulfonyloxy group in 3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-β-L-idofuranose with azide anion, and (2) nucleophilic opening of the oxetan ring of 3,5-anhydro-1,2-*O*-isopropylidene-β-L-idofuranose with azide anion followed by hydrogenation.

This laboratory has been interested in the synthesis of 5-thio- and 5-aminofuranose sugars[2-9] which can be cyclized under acetolysis conditions to the pyranose sugars in which the ring heteroatom is either sulfur or nitrogen. The SN2 displacement of the sulfonyloxy group in the appropriate 5-*O*-*p*-tolylsulfonyl derivative with nucleophiles or nucleophilic opening of the oxetan ring offers convenient routes for the placement of sulfur or nitrogen at C-5. Both of these synthetic methods for introducing an amino group at C-5 of a D-glucofuranose derivative are described.

In the first procedure the *p*-tolylsulfonyloxy group in 3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-β-L-idofuranose[9] (I) is displaced with azide anion in refluxing *N*,*N*-dimethylformamide (DMF) to give a 65% yield of 5-azido-3,6-di-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (II). The infrared spectrum of II in Nujol shows a strong absorption at 2150 cm^{-1}, characteristic of an azide group. The integrated nmr spectrum of compound II in $CDCl_3$ shows a total of 27 protons, ten of which are aromatic (τ 2.5) and six of which represent the isopropylidene methyl protons at 8.53 and 8.7. Other definitive signals in the nmr spectrum are for one anomeric proton as a doublet centered at τ 4.1 (J = 3.5 Hz) and four methylene protons of the benzyl groups at 5.36 and 5.42. It is interesting to note that even in this displacement reaction an 8% yield of the benzyl vinyl ether III (R_f 0.25 in solvent A) is formed by a β-proton elimination, a reaction not seen in other compounds.[10] This observation supports the view of Buchanan and Oakes,[11] who have emphasized that the formation of the olefin XIV and the 3,5-anhydro compound XIII are two independent simultaneous reactions occurring when 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-6-*O*-trityl-α-D-glucofuranose XII is refluxed with sodium methoxide in methanol (Scheme I). The infrared spectrum of III shows a strong absorption at 1650 cm^{-1} (benzyl vinyl ether). The integrated nmr spectrum of III in $CDCl_3$ shows a total of 26 protons, ten of which are aromatic (τ 2.67) and six are for the isopropylidene methyl protons (8.5 and 8.7). Other signals are for an anomeric proton as a doublet centered at τ 4.06 (J = 3.5 Hz), four methylene protons of the benzyl groups at 5.2 and 5.43, and the two vinyl protons at C-6 and C-5 each of unit area, shown as doublets centered at 3.18 (J = 12 Hz) and 4.9 (J = 12 Hz), respectively. The large coupling constant for the vinyl proton signals suggests that the protons are *trans* to each other and that compound III is 3,6-di-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose.

SCHEME I



In addition to the olefin III having an R_f value of 0.25 in solvent A, another olefin with an R_f value of 0.39, suggestive of structure IV or V, is isolated in 6% yield. The nmr spectrum of olefin IV or V in $CDCl_3$ shows a perfect integration for 26 protons, ten of which are aromatic at τ 2.67, six are for the methyls of the isopropylidene and 8.58 and 8.65, and one is for the anomeric C-1 as a doublet centered at 3.88 (J = 3.5 Hz). The other nine protons are spread between τ 5 and 5.83. However, it is significant that there are no vinyl proton signals shown in the usual olefinic proton range of τ 3–5 (except the anomeric proton). Also the methyl proton

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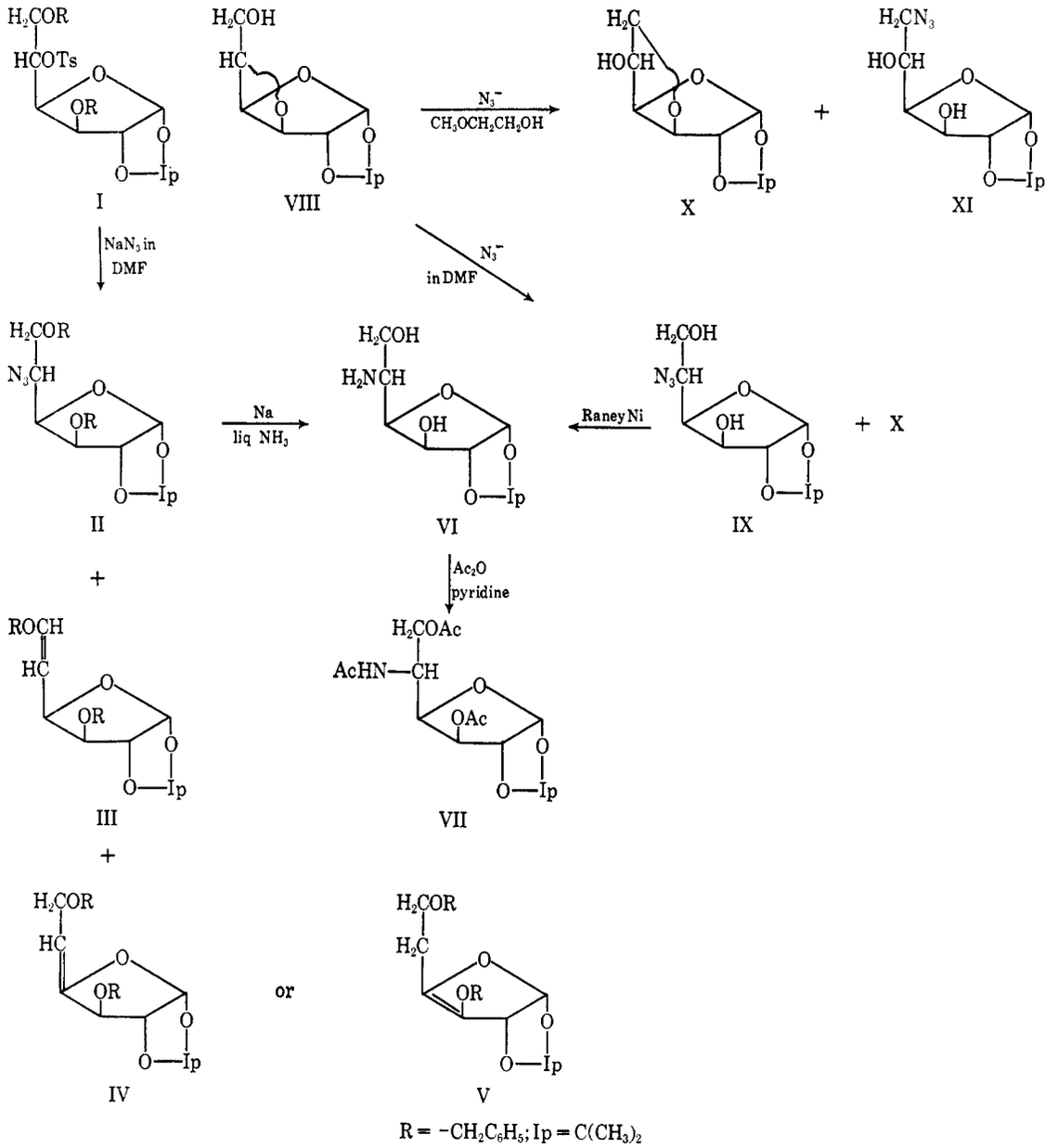
SCHEME II



R = $-CH_2C_6H_5$; Ip = $C(CH_3)_2$

signals of the isopropylidene group have shifted to τ 8.58 and 8.65 from the usual values 8.5 and 8.7, suggestive of the presence of a double bond allylic to the isopropylidene acetal group, in which case it can shield one of the methyl groups of the isopropylidene owing to diamagnetic anisotropy of the double bond. The infrared spectrum of compound IV or V shows a strong olefinic absorption at 1685 cm^{-1}, often mistaken for a carbonyl absorption. Such unusual absorption of the vinyl benzyl ether group has also been observed by other workers.[12-14] Also, it is well known that the exocyclic double bond in methylenecyclopentanes readily isomerizes in the presence of a base to give the stable 1-methylcyclopentene.[15] Whether such a migration from *exo* to *endo* will take place in pentoses is worth investigating, and it is being pursued in this laboratory. These facts suggest that the second olefin (R_f 0.39) is represented by structure V rather than IV which is perhaps first formed by a β-proton elimination but probably isomerizes to V. Both olefins III and V (or IV) absorb bromine from a bromine–carbon tetrachloride solution and decolorize an aqueous potassium permanganate solution.

Reduction of the azido compound (II) with sodium in liquid ammonia (Scheme II) gives an essentially quantitative yield of crystalline 5-amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (VI) which is further characterized through its crystalline triacetyl derivative, 5-acetamido-3,6-di-*O*-acetyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (VII). The infrared spectrum of VII in Nujol shows characteristic absorption peaks at 3255, 3080 (NH), 1760, 1740 (*O*-acetyl), 1660 (amide), and 1225 cm^{-1} (acetate). The integrated nmr spectrum in $CDCl_3$ shows a total of 23 protons, six of which are for the isopropylidene methyl protons at τ 8.49 and 8.68, three for the N-acetyl protons

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at 8.06, and six for the *O*-acetyl protons at 7.88 and 7.92. The anomeric proton, as usual, is shown as a doublet at τ 4.04 (J = 3.5 Hz) and the N–H proton appears as a doublet centered at 3.73 (J = 9 Hz).

Another route to compounds VI and VII is by nucleophilic opening of the oxetan ring of 3,5-anhydro-1,2-*O*-isopropylidene-β-L-idofuranose (VIII). Compound VIII is prepared in a 28% yield, higher than previously reported.[11,16] Instantaneous addition of the theoretical amount or excess of sodium methoxide to a solution of XII favors the formation of the olefin XIV rather than the 3,5-anhydro ring XIII. However, when slightly more than the theoretical amount of sodium methoxide (1.1 molar proportion) in methanol is added dropwise over a period of 45 min a 33% yield of 3,5-anhydro-1,2-*O*-isopropylidene-6-*O*-trityl-β-L-idofuranose (XIII) is obtained. Also, it is found that detritylation of XIII with ethanol–acetic acid–water at 25° for 24 hr produces 3,5-anhydro-1,2-*O*-isopropylidene-β-L-idofuranose (VIII) in 28% yield, which is greater than the yields obtained at higher reaction temperatures.[11]

Nucleophilic ring opening of VIII with azide anion in refluxing DMF–water (19:1) over a period of 7 days gives a 40% yield of 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (IX) and a 15% yield of 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose (X). The base-catalyzed isomerization of VIII to X has been reported previously.[11] Reaction of compound VIII with azide anion in 2-methoxyethanol–water (19:1) does not produce IX but gives a 50% yield of 6-azido-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose[17] (XI) and a 10% yield of X. These findings are in agreement with the results obtained by Buchanan and Oakes.[11]

Reduction of IX with Raney nickel in absolute ethanol produces a crystalline VI, which is further characterized by its acetate VII.

Experimental Section

Analytical Methods.—Purity of products was determined by thin layer chromatography (tlc) on silica gel G[18] coated glass plates (5 × 13 cm) irrigated with A, hexane–ethyl acetate (6:1); B, chloroform–methanol (6:1); C, chloroform–acetone (9:4); D, benzene–ethyl acetate (2:1); and E, chloroform–acetone (9:1). Solvent ratios are based on volumes. Components were located by spraying with 5% sulfuric acid in ethanol and heating until permanent char spots were visible. Melting points are corrected and were determined on a Fisher-Johns apparatus. Nuclear magnetic resonance spectra were obtained with a Varian Associates A-60 instrument. Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer. Evaporations were done under reduced pressure with a bath temperature below 40°. Adsorption chromatography was made on silica gel[19] and neutral alumina (Woelm). Comparison of materials with authentic compounds was made by mixture melting point determination, infrared and nmr spectra, and thin layer chromatography.

3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-β-L-idofuranose (I).—This compound was prepared from 3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-β-L-idofuranose according to literature procedure.[9] The latter compound after two recrystallizations from ether–hexane had mp 75–76°, $[\alpha]^{25}D$ −44.5° (*c* 2, $CHCl_3$). Compound I was recrystallized from ether and had mp 89–90°, $[\alpha]^{25}D$ −15.8° (*c* 2, $CHCl_3$). *Note:* In an earlier report[9] the melting points of these two compounds were erroneously reversed.

5-Azido-3,6-di-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (II).—Compound I (1 g) was refluxed in 25 ml of DMF containing sodium azide (1 g) for 16 hr with the exclusion of moisture. The reaction mixture was cooled and diluted with 150 ml of dry xylene. The precipitated salts were removed by filtration and the filtrate was concentrated under reduced pressure to a thick syrup (655 mg). Column chromatography of this syrup (eluent A), on silica gel separated the azide II and compounds III and IV or V. The azide fractions (R_f 0.35) were collected and concentrated under reduced pressure whereupon 5-azido-3,6-di-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (II, 500 mg, 65% of theory) solidified. Compound II was recrystallized from petroleum ether (bp 60–80°) as needles: mp 71°, $[\alpha]^{25}D$ −37.5 (*c* 1, $CHCl_3$). Infrared spectrum in Nujol showed a strong azide absorption at 2150 and at 700 and 755 cm^{-1} (monosubstituted phenyl).

Anal. Calcd for $C_{23}H_{27}N_3O_5$: C, 64.92; H, 6.40; N, 9.88. Found: C, 64.91; H, 6.40; N, 9.80.

The fractions which contained the slower running spot (R_f 0.25), compound III, were collected and concentrated to yield 53 mg (8% of theory), $[\alpha]^{25}D$ −68.6° (*c* 2.14, $CHCl_3$). The ir spectrum of III showed a strong benzyl vinyl ether absorption at 1650 cm^{-1}. The fractions having R_f 0.39 were collected and concentrated to yield 40 mg of IV or V (6% of theory), $[\alpha]^{25}D$ −33.2° (*c* 2.32, $CHCl_3$). The ir spectrum showed a strong olefinic absorption at 1685 cm^{-1}.

5-Amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (VI).—A solution of compound II (375 mg) in 10 ml of dry 1,2-dimethoxyethane was added to 50 ml of liquid ammonia. To this solution, under stirring, were added small pieces of freshly cut sodium, one at a time, until the blue color of the solution persisted for more than 10 min. The reaction mixture was then decomposed with excess ammonium chloride and the ammonia was allowed to evaporate. The residue was extracted with dimethoxyethane and filtered. The filtrate was concentrated under reduced pressure to a viscous syrup (200 mg) which had a faint odor of bibenzyl. It was chromatographed on silica gel using eluent B. The effluents of the amino sugar (VI) were collected and concentrated to a gritty material (190 mg) which, after recrystallization from ethyl acetate, had mp 125–126°, $[\alpha]^{25}D$ −13.75° (*c* 4, methanol).

Anal. Calcd for $C_9H_{17}NO_5$: C, 49.30; H, 7.82; N, 6.39. Found: C, 49.41; H, 7.85; N, 6.36.

5-Acetamido-3,6-di-*O*-acetyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (VII).—Compound VI (190 mg) was acetylated with 2 ml of dry pyridine and 1 ml of acetic anhydride. Acetylation was complete in 1 hr. The reaction mixture was poured into an ice-cold solution of sodium bicarbonate (3 g in 100 ml). After standing for 1 hr, the solution was extracted with two 50-ml portions of chloroform. The chloroform extract was washed twice with water and after drying over anhydrous sodium sulfate was concentrated to a syrup. The residue, which had a faint odor of pyridine, was dissolved in 50 ml of toluene and evaporated under reduced pressure whereupon the residue solidified; it was recrystallized from ether to give needles: yield 210 mg; mp 145–146°; $[\alpha]^{25}D$ +1.3° (*c* 6, $CHCl_3$). The infrared spectrum in Nujol showed absorption peaks at 3255, 3080 (NH), 1760, 1740 (*O*-acetyl), 1660 (amide), and 1225 cm^{-1} (acetate).

Anal. Calcd for $C_{15}H_{23}NO_8$: C, 52.17; H, 6.71; N, 4.05. Found: C, 52.16; H, 6.72; N, 4.09.

3-*O*-Acetyl-1,2-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-6-*O*-triphenylmethyl-α-D-glucofuranose (XII).—Compound XII was prepared following published directions in 81% yield.[16]

3,5-Anhydro-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-β-L-idofuranose (XIII) and 3,5-Anhydro-1,2-*O*-isopropylidene-β-L-idofuranose (VIII).—To a stirred refluxing solution of compound XII (65.8 g, 0.1 mol) in 250 ml of dry methanol was added dropwise, over a 45-min period, a freshly prepared solution of sodium methoxide in methanol (2.53 g of sodium in 50 ml of methanol). The reaction mixture was refluxed for 45 min and cooled, and the methanol was removed under reduced pressure whereupon the residue solidified. The residue was triturated with 700 ml of dry ether, and the mixture was filtered. The filtrate was washed twice with 100 ml of water. After drying over anhydrous sodium sulfate, ether was removed and the residue was taken into 200 ml of hot chloroform. The chloroform solution was diluted with petroleum ether (bp 60–80°) to about 800 ml whereupon 5-deoxy-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-

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(19) J. T. Baker Chemical Co., Phillipsburg, N. J.

α-D-*xylo*-hex-5-enofuranose (XIV) crystallized. The mixture was cooled in ice for 1 hr, and compound XIV was separated by filtration. The filtrate was concentrated and the above process of crystallization was repeated with 50 ml of chloroform and 350 ml of petroleum ether. The filtrate after separation of a second batch of compound XIV was concentrated to a pale yellow syrup (20 g). The syrup was then chromatographed over a neutral alumina (100 g) column prepared in benzene. Elution with benzene gave 3,5-anhydro-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-β-L-idofuranose (XIII, 15 g, 33%) which was chromatographically homogeneous by tlc. Compound XIII was then detritylated by stirring at 25° for 24 hr its solution in 35 ml of ethanol, 75 ml of acetic acid, and 18 ml of water. The reaction mixture was cooled to −15° and filtered after 12 hr to remove triphenylmethanol. The filtrate was concentrated to a syrup which was dissolved in 200 ml of chloroform. The chloroform solution was washed with aqueous sodium bicarbonate followed by water. The chloroform solution was dried over anhydrous sodium sulfate and was filtered, and the filtrate was concentrated to a pale yellow syrup (7 g) which was chromatographed over silica gel using eluent C. The proper effluents were collected and concentrated, whereupon compound VIII spontaneously crystallized, mp 50° (yield 5.6 g, 28% of theory).

5-Azido-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (IX).—To a solution of compound VIII (1 g) in 95 ml of DMF was added a slurry of 5 g of sodium azide in 5 ml of water. The mixture was refluxed gently for 7 days. The reaction mixture was cooled, 300 ml of xylene was added, and the mixture was filtered. The filtrate was then concentrated to dryness. The residue was triturated with 100 ml of xylene, and the mixture was filtered. The filtrate was concentrated to a reddish orange syrup (800 mg) which was chromatographed over silica gel using eluent D. The proper fractions (faster running component) were collected and concentrated to a syrup (670 mg) which was again chromatographed over silica gel using eluent E. The fractions containing the faster running component were collected and concentrated whereupon it crystallized spontaneously (150 mg). After recrystallization from ether–hexane, needles were obtained, mp 56°. It was identified as 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose X (lit.[20] mp 56–57°). The fractions which contained the slower running spots containing the azide (IX) were combined and concentrated to a pale yellow syrup (470 mg, 40% of theory) $[\alpha]^{25}D$ −10.55° (*c* 2.18, $CHCl_3$), which showed a strong absorption at 2150 cm^{-1} (azide) in the infrared spectrum. In a similar reaction, compound VIII was refluxed with sodium azide in 2-methoxyethanol–water (19:1) for 24 hr. On isolation in the same way as above a 50% yield of 6-azido-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (XI), mp 108°, was obtained. No change in melting point occurred in a mixture with an authentic sample.[17]

5-Amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (VI) and 5-Acetamido-3,6-di-*O*-acetyl-5-deoxy-α-D-glucofuranose (VII).—Compound IX (470 mg) in 25 ml of absolute ethanol containing about 2 g of Raney nickel was hydrogenated at 25° for 2 hr. The reaction mixture, worked up in the usual way, gave a pale yellow syrupy compound VI which had the same R_f in irrigant B as compound VI prepared by the earlier method. It was recrystallized from ethyl acetate, mp 125–126°. Acetylation of VI by the usual procedure gave 5-acetamido-3,6-di-*O*-acetyl-5-deoxy-α-D-glucofuranose (VII) (450 mg) as needles, mp 145–146°. The infrared and nmr spectra were identical with those of compound VII prepared by the method described above. The mixture melting point was undepressed.

Registry No.—II, 16958-26-2; VI, 16958-27-3; VII, 16958-28-4.

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Selective Cleavage of the Glycosidic Bond in Acetylated 2-Acetamido-2-deoxy-β-D-glucopyranosides by a Chemical Transglycosylation

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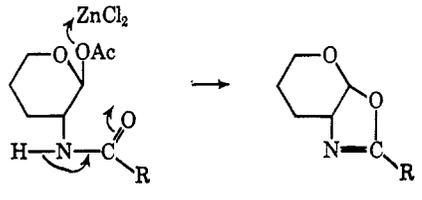
The anchimeric assistance afforded by acylamino groups to nucleophilic displacements on neighboring carbon atoms suggests that derivatives of 2-acylamino-2-deoxyaldoses with a *trans* arrangement of the groups at C-1–C-2 may be more susceptible than other aldose derivatives to the action of certain cleaving reagents. Since it has been shown that acetic anhydride–zinc chloride converts 2-acylamino-2-deoxyaldoses into oxazolines, and, since such oxazolines undergo reaction with alcohols to give glycosides, the behavior of a number of acetylated aldose derivatives with zinc chloride–benzyl alcohol has been investigated. In each case, the reaction has been conducted in butyl acetate solution at 125° for varying times. Under these conditions, 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (1) is rapidly converted into benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**3**) in high yield; its anomer, **4**, reacts much more slowly, giving **3** and a small amount of the anomeric benzyl glycoside **5**. The *trans* glycoside methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**6**) is readily cleaved to a mixture of **3** and **5** but its *cis* anomer **7** is not attacked. Likewise, methyl β-D-glucopyranoside tetraacetate (**8**) is stable under these reaction conditions. The glycosidic bond in the β-linked disaccharide derivative, chitobiose octaacetate (**9**), is slowly attacked by the reagent to give (after reacetylation) **3** and **5** but, under the conditions employed, compounds which appear to be the acetylated derivatives of the anomeric benzyl glycosides of the disaccharide (α and β **11**) were also obtained. The potential utility of this apparently selective solvolysis for the investigation of the structures of oligosaccharides is pointed out.

A recent investigation in this laboratory[2] has shown that the acetylation of 2-acylamino-2-deoxyaldoses with acetic anhydride and anhydrous zinc chloride can give rise to the formation of acetylated oxazolines. This reaction may be construed as a combination of two reactions: in the first, normal acetylation takes place and, in the second, an acetoxy group at C-1 is displaced with the formation of an oxazoline. It seems reasonable to assume that the latter reaction proceeds by the mechanism portrayed in eq 1 and that the marked



(1)

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