Anal. Calcd for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 47.70; H, 7.11.

1,4,5-Tri-*O*-acetyl-2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (XI).—Acetylation of X (36 mg) gave a 62% yield of crystalline triacetate. The long needles, recrystallized twice from chloroform–pentane, melted at 63–65°, $[\alpha]^{20}D$ −98.3° (*c* 0.3, chloroform).

Anal. Calcd for $C_{13}H_{18}O_8$: C, 51.65; H, 6.00. Found: C, 51.74; H, 6.13.

Sodium Periodate Oxidations.—The sodium periodate oxidations were carried out on a microscale employing the method described by Dixon and Lipkin.[25] A Beckman DU spectrophotometer was used to determine the amount of oxidant consumed by the measurement of the absorption of periodate ion at a wavelength of 222.5 mμ. Methyl 4,6-*O*-benzylidine-α-D-glucopyranoside consumed 0.32 and 0.67 mole of periodate per mole of compound in 18 and 88 hr, respectively, whereas 4-*O*-tosylsedoheptulosan (IV) and 2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (X) were not oxidized under similar conditions.

Lead Tetraacetate–Pyridine Oxidations.—The method of Goldschmid and Perlin[22] was slightly modified by using a commercial grade of lead tetraacetate which was merely dried by being pressed between layers of filter paper until the first signs of decomposition were observed. It was then immediately dissolved in a minimum amount (about 65 parts) of dry pyridine forming a very dark solution. This reagent was tested on 10-mg samples of the triacetate (II) and montosylate (IV) of sedoheptulosan and on 2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (X) at 5°. Only X reacted, consuming 0.76 mole of oxidant within 6.5 hr. After 24 hr, overoxidation was noted but the other two compounds were still unreactive.

Reaction of 2,7-Anhydro-3-*S*-methyl-3-thio-β-D-*gluco*-heptulopyranose (VIII) with Acid.—Paper chromatography of the reaction of 170 mg of VIII in 5 ml of 0.2 *N* sulfuric acid at 85° for 7 hr indicated the formation of a new compound whose mobility was slightly slower than that of the starting material. The resulting syrup reduced Fehling solution and upon acetylation yielded a crystalline product which could not be purified. After several recrystallizations from ethyl alcohol–pentane, the needles melted at 112–123°. Although decomposition was not evident, the compound on being heated at various high temperatures gave erratic carbon analyses and weight losses ranged as high as 33%. Elemental analysis of a sample dried at 80° overnight (25% weight loss) indicated that the compound might be the penta-acetate of 3-*S*-methyl-3-thio-D-*gluco*-heptulopyranose contaminated with some starting material.

Anal. Calcd for $C_{18}H_{26}O_{11}S$: C, 47.99; H, 5.82; S, 7.12. Found: C, 48.30; H, 5.87; S, 7.77.

Registry No.—II, 7540-81-0; VIII, 7485-52-1; 2,7-anhydro-β-D-mannoheptulopyranose, 7739-21-1; III, 7785-14-0; IV, 10026-48-9; VII, 7739-22-2; IX, 7739-23-3; X, 7782-05-0; XI, 7739-24-4.

Acknowledgment.—The author wishes to thank the Section on Microanalytical Services and Instrumentation of this laboratory for the microanalyses, infrared spectra, and nmr spectra, and especially Dr. W. C. Alford for the sodium periodate determinations.

(25) J. S. Dixon and D. Lipkin, *Anal. Chem.*, **26**, 1092 (1954).

Syntheses with Partially Benzylated Sugars. VII.[1] The Anomeric Vinyl D-Glucopyranosides

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Two synthetic pathways to the synthesis of vinyl D-glucopyranosides have been explored. In the first pathway, 2-chloroethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside was converted into *N*-(2-β-D-glucopyranosyloxyethyl)dimethylammonium chloride (I) and thence into 2-dimethylaminoethyl β-D-glucopyranoside (V). The latter base was quaternized with methyl iodide and the resulting iodide (VI), after conversion into the hydroxide, was subjected to a Hofmann degradation. Acetylation of the crude product afforded crystalline vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII). Hydrogenation of VIII gave the known ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (XII). An attempted synthesis of vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII) through the Cope degradation of the *N*-oxide of 2-dimethylaminoethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (III) was unsuccessful. The second pathway to the synthesis of the vinyl D-glucopyranosides began with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (IX); an improved preparation of this substance from methyl α-D-glucopyranoside is described. Transvinylation of IX with isobutyl vinyl ether in the presence of mercuric acetate readily gives the anomeric vinyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosides (X and XI) separable by chromatography. The structures of these substances were demonstrated by conversion into the known ethyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosides (XII and XIII). The rates of hydrolysis of the two vinyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosides (X and XI) under acidic conditions were measured and the axial anomer was found to be cleaved more rapidly than the equatorial anomer. The benzyl groups of X and XI were removed through the action of sodium in liquid ammonia and the immediate products were acetylated to give the anomeric vinyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosides (VIII and XIV), both in crystalline form. From these, the two anomeric vinyl D-glucopyranosides (XV and XVI) were prepared, only the α anomer (XVI) being obtained in crystalline form. Like phenyl α-D-glucopyranoside, vinyl α-D-glucopyranoside (XVI) is comparatively stable to alkali; its anomer (XV) resembles phenyl β-D-glucopyranoside in that it is converted into 1,6-anhydro-β-D-glucopyranose (XVII) when treated with alkali.

In view of the number and diversity of the D-glucose derivatives which have been described in the literature, it may seem, *a priori*, somewhat surprising that one of the simplest of these, vinyl D-glucopyranoside, has not, apparently, attracted the attention of organic chemists. However, when one considers, on the one hand, the nature of the conventional procedure for the vinylation of alcohols (*i.e.*, acetylene or vinyl chloride with an alkali at elevated temperatures and pressures[4-6]) and, on the other hand, the well-known

(1) Paper VI of this series: T. D. Inch and H. G. Fletcher, Jr., *J. Org. Chem.*, **31**, 1810 (1966).

(2) Scientist in the Visiting Program of the National Institutes of Health, July 1962 to June 1965.

(3) The initial portion of the investigation described in this paper was undertaken by two of us (T. D. P. and J. K.) while at the Rocky Mountain Laboratory of the National Institute of Allergy and Infectious Diseases, Hamilton, Mont.

(4) J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold Publishing Corp., New York, N. Y., 1954, p 126.

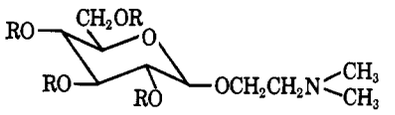
(5) C. E. Schildknecht, A. O. Zoss, and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947).

(6) W. Reppe, *Ann.*, **601**, 81 (1956).

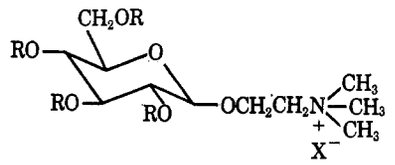
vulnerability toward alkali of aldoses which are unsubstituted at C-1, this hiatus in the chemical literature becomes readily understandable.[7]

In view of the unsuitability of traditional vinylation procedures for the synthesis of the vinyl D-glucopyranosides, we initially turned our attention to an indirect approach, involving the introduction of a double bond in a preformed and suitably substituted ethyl D-glucopyranoside. Of the various reactions available for the formation of a double bond in an aglucon, the degradations of Hofmann and of Cope[8] appeared to be the most attractive. The known 2-chloroethyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside[9] was therefore converted, through the action of dimethylamine, into *N*-(2-β-D-glucopyranosyloxyethyl)dimethylammonium chloride (I). The four hydroxyl groups of I were masked by acetylation to give *N*-[2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)ethyl]dimethylammonium chloride (II) and this, in turn, was converted into the free tertiary amine (III). Attempts to convert the latter compound into its *N*-oxide and thence, *via* the Cope degradation and acetylation to vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII) were unsuccessful.[10] The structure of III was confirmed through conversion into the known[9,11] *N*-[2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)ethyl]trimethylammonium chloride (IV, "β-tetraacetylcholine chloride *d*-glucoside").

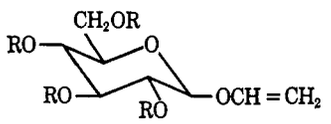
Attention was then turned to a synthetic pathway involving the Hofmann degradation. The free base, 2-dimethylaminoethyl β-D-glucopyranoside (V), prepared from I, was converted into the quaternary iodide (VI) through the action of methyl iodide. The structure of VI was confirmed by conversion into the known[9,11] chloride (VII). Silver carbonate was used to convert VI into the quaternary ammonium hydroxide which, without isolation, was pyrolyzed directly; subsequent acetylation yielded crystalline vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII) in 29% yield (based on VI). In acidic solution VIII readily gave the 2,4-dinitrophenylhydrazone of acetaldehyde; a quantitative hydrogenation over platinum black converted VIII into the well-known ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (XII).[12] These reactions proved that the crystalline product obtained



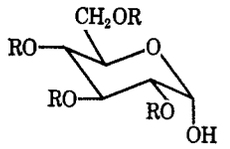
I, R = H; hydrochloride
II, R = CH_3CO; hydrochloride
III, R = CH_3CO
V, R = H



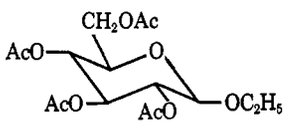
IV, R = CH_3CO; X = Cl
VI, R = H; X = I
VII, R = H; X = Cl



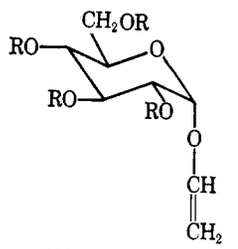
VIII, R = CH_3CO
X, R = $C_6H_5CH_2$
XV, R = H



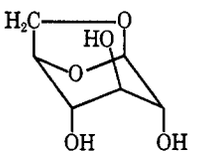
IX, R = $C_6H_5CH_2$



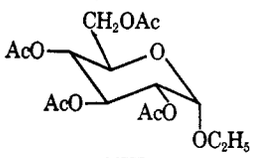
XII



XI, R = $C_6H_5CH_2$
XIV, R = CH_3CO
XVI, R = H



XVII



XIII

through the Hofmann degradation was indeed vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII).

The above-described pathway to VIII is undeniably laborious and entails substantial losses of material, the over-all yield being low. We therefore sought an alternative synthetic procedure, preferably one which would yield the anomeric vinyl D-glucopyranosides simultaneously. Watanabe and Conlon[13] showed that alcohols may be converted into the corresponding vinyl ethers by transetherification with commercially available vinyl ethers in the presence of mercuric salts of weak acids such as mercuric acetate. In the carbohydrate field this vinylation procedure has been used by Barker, *et al.*,[14] to effect the partial vinylation of sucrose and by Black, Dewar, and Rutherford[15] to prepare 1,2:5,6-di-*O*-isopropylidene-3-*O*-vinyl-α-D-glucofuranose. In neither of these cases, of course, was a reducing sugar derivative involved. Treatment

(7) Reppe[6] noted that the vinylation of mono- and disaccharides was uniformly unsuccessful and, as far as we are aware, the only successful vinylation of a reducing carbohydrate derivative is that of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose, reported recently by B. I. Mikhant'ev and V. L. Lapenko: *TV. Lab. Khim. Vysokomolekul. Soedin. Voronezhsk. Univ.*, 40 (1963); *Chem. Abstr.*, **63**, 11677 (1965). The vinylation of nonreducing carbohydrate derivatives was studied by Reppe[6] and has been the subject of extensive investigations carried out by B. I. Mikhant'ev and his associates; *cf.* B. I. Mikhant'ev and V. L. Lapenko, *Zh. Obshch. Khim.*, **31**, 1843 (1961); B. I. Mikhant'ev, V. L. Lapenko, and L. P. Pavlov, *ibid.*, **32**, 2505 (1962); B. I. Mikhant'ev and V. L. Lapenko, *ibid.*, **34**, 694 (1964). The vinylation of methyl α-D-glucopyranoside with acetylene and with vinyl chloride has been studied by A. J. Deutschman and H. W. Kircher [*J. Am. Chem. Soc.*, **83**, 4070 (1961)] while R. L. Whistler, H. P. Panzer, and J. L. Goatley [*J. Org. Chem.*, **27**, 2961 (1962)] have vinylated 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose.

(8) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

(9) E. L. Jackson, *J. Am. Chem. Soc.*, **60**, 722 (1938).

(10) Several years subsequent to this study, D. J. Cram, M. R. V. Sahyun, and G. R. Knox [*J. Am. Chem. Soc.*, **84**, 1734 (1962)] noted that in dry dimethyl sulfoxide or dry tetrahydrofuran the Cope degradation may proceed at a practicable rate at 25°. It is possible that these conditions, far milder than those used in the present research, may be suitable for the conversion of the *N*-oxide of III into VIII.

(11) H. W. Coles and F. H. Bergeim, *ibid.*, **60**, 1376 (1938).

(12) J. H. Ferguson, *ibid.*, **54**, 4086 (1932).

(13) W. H. Watanabe and L. E. Conlon, *ibid.*, **79**, 2828 (1957).

(14) S. A. Barker, J. S. Brimacombe, M. R. Harnden, and J. A. Jarvis, *J. Chem. Soc.*, 3403 (1963).

(15) W. A. P. Black, E. T. Dewar, and D. Rutherford, *ibid.*, 4433 (1963); *Chem. Ind.* (London), 1624 (1962).

of any reducing sugar derivative with mercuric acetate would appear to involve the hazard of oxidation, for Dorofeenko[16] has shown that this reagent effectively converts the common aldoses into aldonic acids and, indeed, both Dorofeenko[16] and Stoodley[17] have found that alditols are oxidized to ketoses through the action of mercuric acetate. It was therefore deemed advisable to choose for transvinylation a D-glucopyranose derivative masked at positions 2, 3, 4, and 6 with comparatively stable substituents and, moreover, a D-glucopyranose derivative which might be relatively resistant to oxidation at C-1. 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranose (IX), first prepared by Schmidt, Auer, and Schmadel,[18] appeared to fulfill these requirements. The substance appears to be comparatively resistant to the action of a variety of common oxidants, even of bromocarbamide which Vaterlaus, Kiss, and Spiegelberg[19] found to be suitable for the oxidation of 3,5,6-tri-*O*-benzyl-2-*O*-methyl-D-glucofuranose to 3,5,6-tri-*O*-benzyl-2-*O*-methyl-D-glucono-γ-lactone.[20] In the course of the present research the preparation of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (IX) from the inexpensive and commercially available methyl α-D-glucopyranoside was restudied and a comparatively simple process, giving IX in 63% yield, was developed.[21]

The reaction of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (IX) with a large excess of boiling isobutyl vinyl ether in the presence of mercuric acetate was conveniently followed by thin layer chromatography. After 8 hr a single product, migrating at a faster rate than the starting material, was detected; after a longer reaction time (18 hr) all of the starting material was consumed and, in addition to the first product, a second, of similar chromatographic properties, was present.[22] Both products were unsaturated as shown clearly by a permanganate spray. Preparative column chromatography served to separate the two products; one, the major product, was obtained as a syrup of $[\alpha]^{20}D$ +30.9° in chloroform and the other, the minor product, as crystals of $[\alpha]^{20}D$ +10.9° in chloroform. Both substances gave infrared spectra with features characteristic of vinyl ethers and elementary analysis afforded values consistent with a vinyl tetra-*O*-benzylhexoside. Catalytic reduction of the more dextrorotatory isomer gave a product whose trimethylsilyl ether proved to be chromatographically indistinguishable from the trimethylsilyl derivative of ethyl α-D-glucopyranoside; acetylation of the reduction product afforded the known[12] crystalline ethyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (XIII). In a similar fashion, the less dextrorotatory product was converted into the known[12] ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside. On the basis of this evidence, the major product of the vinylation of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (IX) is vinyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (XI) while the minor product is the corresponding β anomer (X).

It will be recalled that alkyl glucopyranosides with an equatorial aglucon are hydrolyzed more rapidly than the corresponding axial anomers and that the situation is reversed with the phenyl glucopyranosides.[23] It is of interest, then, to note that the acidic hydrolysis (in aqueous dioxane) of vinyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (XI) is some 7.7 times as fast as that of its β anomer (X) and that, in this respect, these anomers resemble the phenyl glucopyranosides rather than the alkyl glucopyranosides. Whether this resemblance is due to mechanistic features in common remains, of course, uncertain.

Removal of the benzyl groups from the two anomeric vinyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosides (X and XI) was effected through the action of sodium in liquid ammonia, a debenzylation technique described recently by Reist, Bartuska, and Goodman.[24] The crude vinyl glucopyranoside (XVI) obtained from XI was acetylated to yield crystalline vinyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (XIV); catalytic deacetylation of XIV with barium methoxide gave crystalline vinyl α-D-glucopyranoside (XVI). In a similar fashion, X gave crystalline vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII), identical with the preparation made from VI through the Hofmann degradation as described earlier. Vinyl β-D-glucopyranoside (XV), made through deacetylation of its tetraacetate (VIII), was obtained as a chromatographically pure syrup with the appropriate elementary composition.

The two anomeric phenyl D-glucopyranosides show highly contrasting behavior in the presence of strong alkali, the α anomer being comparatively stable while the β anomer eliminates the elements of phenol, giving 1,6-anhydro-β-D-glucopyranose (XVII).[25] It was of interest to see whether the two vinyl D-glucopyranosides (XV and XVI) would behave in an analogous fashion. The tetraacetate of the β anomer (VIII) was treated with hot, aqueous potassium hydroxide; the product, after trimethylsilylation, was examined by gas–liquid partition chromatography. On a rough quantitative basis VIII was found to have produced 1,6-anhydro-β-D-glucopyranose (XVII) in 50% yield. A similar treatment of XIV with hot alkali produced no 1,6-anhydro-β-D-glucopyranose (XVII) detectable by gas–liquid partition chromatography. The analogy between the vinyl and the phenyl D-glucopyranosides, at least in respect to behavior with alkali, is therefore apparent. In passing, it may be noted that vinyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (XI) was found to be comparatively stable in alkaline solution; its anomer (X) was not investigated in this respect.

(16) G. N. Dorofeenko, *Ukr. Khim. Zh.*, **27**, 114 (1961); *Chem. Abstr.*, **55**, 20970 (1961).

(17) R. J. Stoodley, *Can. J. Chem.*, **39**, 2593 (1961).

(18) O. T. Schmidt, T. Auer, and H. Schmadel, *Ber.*, **93**, 556 (1960).

(19) B. P. Vaterlaus, J. Kiss, and H. Spiegelberg, *Helv. Chim. Acta*, **47**, 381 (1964); J. Kiss, *Chem. Ind.* (London), 73 (1964).

(20) A later paper in this series will, however, describe the facile oxidation of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose through the action of dimethyl sulfoxide and acetic anhydride.

(21) The procedure is a modification of that developed by M. E. Tate and C. T. Bishop, *Can. J. Chem.*, **41**, 1801 (1963). J. Gigg and R. Gigg [*J. Chem. Soc.*, 82 (1966)] have described a most ingenious and elegant synthesis of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose, involving as an intermediate a mixture of the two anomeric allyl D-glucopyranosides. While the general process which they describe is a valuable addition to the methods of synthesis in the carbohydrate field, it is somewhat more laborious for the preparation of IX than the process described here, because of the commercial availability of methyl α-D-glucopyranoside.

(22) Free mercury was also formed. No evidence for the formation of an oxidized glucose derivative (*i.e.*, 2,3,4,6-tetra-*O*-benzyl-D-glucono-γ-lactone) was obtained, however.

(23) B. Capon and W. G. Overend, *Advan. Carbohydrate Chem.*, **15**, 33 (1960).

(24) E. J. Reist, V. J. Bartuska, and L. Goodman, *J. Org. Chem.*, **29**, 3725 (1964).

(25) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson, *J. Am. Chem. Soc.*, **65**, 3 (1943).

Experimental Section[26]

N-(2-β-D-**Glucopyranosyloxyethyl)dimethylammonium Chloride** (I).—2-Chloroethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside[9] (6 g) was heated with dimethylamine (50 g) in a sealed tube at *ca.* 70° for 5 days. The excess of dimethylamine was then removed and the residue was washed successively with ether and chloroform. Repeated crystallization of the resulting product from ethanol afforded pure *N*-(2-β-D-glucopyranosyloxyethyl)-dimethylammonium chloride (I) in yields varying from 70 to 80%: mp 159–160° (after initially melting below 90°); $[\alpha]^{28}D$ −12° (*c* 1.0, ethanol), −18.8° (*c* 2.1, water).

Anal. Calcd for $C_{10}H_{22}ClNO_6$ (287.75): C, 41.74; H, 7.71; N, 4.87. Found: C, 41.86; H, 7.72; N, 4.82.

N-[2-(**2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)ethyl]dimethylammonium Chloride** (II).—*N*-(2-β-D-Glucopyranosyloxyethyl)dimethylammonium chloride (I, 10 g) was refluxed in a mixture of pyridine (150 ml) and acetic anhydride (20 ml) for 15 min. After the reaction mixture was cooled, the product was precipitated through the addition of ether: 14.4 g (91%), mp 210–212° (*in vacuo*). Recrystallized from aqueous ethanol by the addition of ether, the tetraacetate (II) was obtained as flat plates which readily sublimed as long needles: mp 195–196°, $[\alpha]^{23}D$ −20.7° (*c* 1.25, water).

Anal. Calcd for $C_{18}H_{30}ClNO_{10}$ (455.91): C, 47.42; H, 6.63; Cl, 7.78. Found: C, 47.60; H, 6.80; Cl, 7.75.

A triacetate, rather than the tetraacetate (II), is formed when I is acetylated under milder conditions. In one experiment, I (5.8 g) was acetylated with pyridine (60 ml) and acetic anhydride (30 ml) at room temperature for 2 hr. The solution was concentrated *in vacuo* to a solid mass which was successively extracted with ether and petroleum ether (bp 40–60°) to leave a white solid (8.8 g). Extraction of this material with chloroform afforded II; the chloroform-insoluble portion (3.5 g, 42%) was recrystallized from aqueous ethanol. In an open capillary the substance sublimes, without melting, at 230–278°; *in vacuo* it darkens at 292° and melts at 305°. The infrared spectrum of the substance shows strong absorption at 3226 cm^{-1} (OH). In water the material shows $[\alpha]^{23}D$ +17.7° (*c* 1.02); in methanol it shows $[\alpha]^{23}D$ +19.9° (*c* 1.77).

Anal. Calcd for $C_{16}H_{28}ClNO_9$ (413.87): C, 46.43; H, 6.82; Cl, 8.57; CH_3CO, 31.20. Found: C, 46.27; H, 6.79; Cl, 8.43; CH_3CO, 28.0.

On deacetylation with sodium methoxide and subsequent treatment with hydrochloric acid, the substance gave I, mp 159–160°, $[\alpha]^{23}D$ −11.8° (*c* 1.0, ethanol); the identity of I prepared by this method was confirmed by conversion to the methiodide (VI, described later in this paper), mp 143–144°. The evidence obtained indicates that this product, obtained through the acetylation of I under comparatively mild conditions, is an *N*-[2-(tri-*O*-acetyl-β-D-glucopyranosyloxy)ethyl]dimethylammonium chloride.

2-Dimethylaminoethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (III).—The hydrochloride II (0.5 g) was dissolved in chloroform and the solution was shaken with 1 ml of 5 *N* sodium carbonate, moisture was removed with solid potassium carbonate, and the chloroform solution was concentrated to a colorless syrup which crystallized after sublimation, and was resublimed, or alternatively, recrystallized from ether–petroleum ether to give the free base: 0.3 g (67%); mp 59–60°; $[\alpha]^{25}D$ −19.9° (*c* 2.34, chloroform), −20.3° (*c* 1.08 water).

Anal. Calcd for $C_{18}H_{29}NO_{10}$ (419.42): C, 51.54; H, 6.97; CH_3CO, 41.05. Found: C, 51.75; H, 6.74; CH_3CO, 41.17.

N-[2-(**2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)ethyl]trimethylammonium Chloride** (IV).—The tertiary amine III was dissolved in acetone and an excess of methyl iodide was added. When precipitation of the methiodide was complete, it was removed by filtration and recrystallized from absolute ethanol as fine needles: mp 209–210°, $[\alpha]^{25}D$ −19.9° (*c* 1.06, water).

Anal. Calcd for $C_{19}H_{32}INO_{10}$ (561.38): C, 40.65; H, 5.75; I, 22.61. Found: C, 41.05; H, 5.84; I, 21.8.

Judging from these analytical values the **N-[2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxyethyl)] trimethylammonium iodide** thus obtained was not quite pure. The substance was dissolved in water and the solution was stirred with an excess of silver chloride. After removing the silver salts by centrifugation, the solution was concentrated to dryness and the residue was crystallized from ethanol–ether. Dried *in vacuo* over phosphorus pentoxide at 56°, the product had mp 227–229° and $[\alpha]^{25}D$ −25.3° (*c* 1.02, water). *N*-[2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)ethyl]trimethylammonium chloride (IV) is recorded as having mp 230° uncor,[9] mp 217–218°[11] $[\alpha]^{20}D$ −25.6° (water),[8] and −25° (water).[11]

2-Dimethylaminoethyl β-D-Glucopyranoside (V).—The hydrochloride I (10 g) was dissolved in water and the solution was passed through a column of Amberlite IRA-401 (OH^-). The solution was concentrated *in vacuo* (40° bath) and the residue was dissolved in aqueous acetone to give 6.7 g (74%) of crystalline material, mp 84–97°. The product may be sublimed *in vacuo*, though with marked evolution of gas; on standing in the air, the crystalline sublimate turned to a syrup.

Anal. Calcd for $C_{10}H_{21}NO_6 \cdot 0.5H_2O$: mol wt, 260.29. Found: mol wt, 260 (titration with 0.01 *N* HCl).

The sample which had been titrated with hydrochloric acid afforded I, mp 157–159°.

N-(2-β-D-**Glucopyranosyloxyethyl)trimethylammonium Iodide** (VI).—Treatment of V in acetone solution with methyl iodide yielded VI as rosettes. Recrystallized from ethanol, VI was obtained as flat plates: mp 142–144°, $[\alpha]^{27}D$ −20.5° (*c* 1.0, water).

Anal. Calcd for $C_{11}H_{24}INO_6$ (393.23): C, 33.60; H, 6.15; I, 32.29. Found: C, 33.62; H, 6.13; I, 32.57.

N-(2-β-D-**Glucopyranosyloxyethyl)trimethylammonium Chloride** (VII).—An aqueous solution of VI was treated with an excess of silver chloride, the silver salts were removed by centrifugation, and the solution was concentrated *in vacuo* to a colorless glass which showed $[\alpha]^{25}D$ −26.7° (*c* 0.94, water). Jackson[9] reported $[\alpha]^{20}D$ −26.5° (water) for VII.

Vinyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (VIII) **from *N*-(2-β-D-Glucopyranosyloxyethyl)trimethylammonium Iodide** (VI).—The iodide VI (28.7 g, 73 mmoles) was dissolved in water and the solution was treated below 10° with silver carbonate prepared from 12.4 g (73 mmoles) of silver nitrate. After filtration of the solution and concentration *in vacuo*, 23.3 g of solid remained. This residue, placed in a vacuum system with a pumping capacity of 20 l./sec, was heated directly with a free flame. Vigorous gas evolution with some sublimation ensued; near the middle of the decomposition the flask was cooled and the brittle foam was broken up. The pyrolysis was continued and toward the end of the reaction the black, spongy mass which formed was again cooled and was broken up. The crude vinyl β-D-glucopyranoside thus obtained (14.8 g, 98%) was dissolved in a mixture of pyridine (235 ml) and acetic anhydride (55 ml) and the solution was left at 25° for 16 hr. The excess of reactants was removed by concentration *in vacuo* and the resulting thick syrup was extracted repeatedly with ether, Supercel being added to facilitate the extraction. Concentration of the combined extracts afforded 7.8 g (29%, based on VI) of crude vinyl 2,3,4,6-*O*-acetyl-β-D-glucopyranoside which crystallized spontaneously on standing for 2 days. Recrystallized from aqueous acetone, the product had mp 103–104°; sublimed at 1 μ and 100–110° (bath), the vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside had mp 104–104.5° and $[\alpha]^{20}D$ −5.5° (*c* 1.02, chloroform). The material may be recrystallized from acetone–water.

Anal. Calcd for $C_{16}H_{22}O_{10}$ (374.36): C, 51.34; H, 5.92; CH_3CO, 45.99. Found: C, 51.31; H, 6.00; CH_3CO, 43.46 (average of three determinations).

Hydrolysis of a sample of VIII in ethanolic hydrochloric acid in the presence of 2,4-dinitrophenylhydrazine gave acetaldehyde 2,4-dinitrophenylhydrazone; recrystallized from alcohol, this melted at 168° either alone or in admixture with authentic material.

On hydrogenation in methanol solution over platinum black (from 81 mg of platinum oxide), the compound (295 mg, 0.78 mmole) absorbed 0.78 mmole of hydrogen. After removal of the catalyst and solvent, the product was crystallized from aqueous ethanol as platelets, mp 106–107°. The infrared spectrum of the material was identical with that of an authentic sample of **ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside** (XII);[12] a mixture melting point was undepressed.

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranose (IX).—A mixture of methyl α-D-glucopyranoside (75 g), commercial, powdered potassium hydroxide[27] (375 g), and dioxane (275 ml) was efficiently stirred and slowly warmed to the boiling point while benzyl chloride (125 ml) was added dropwise. More benzyl chloride (250 ml) was added dropwise to the boiling and vigorously

(26) Melting points are corrected.

(27) Hooker Chemical Corp., Niagara Falls, N. Y.

stirred mixture, heating and stirring being continued for 2 hr after the addition was complete. The reaction mixture was cooled to *ca.* 70° and steam distilled to remove dioxane, benzyl chloride, and benzyl alcohol.[28] The organic layer was then separated, washed with water, and mixed with glacial acetic acid (3.2 l.) and 4 *N* sulfuric acid (1.8 l.). The hydrolysis mixture was heated on the steam bath with constant stirring for 24 hr, 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (IX) crystallizing out toward the end of this period. Water (800 ml) was added, the mixture was cooled in an ice bath, and the product was removed by filtration. The crystals were washed successively with aqueous acetic acid (400 ml, 50%, v/v), water, and aqueous methanol (400 ml, 75%, v/v) and finally dried yielding 132.3 g (63%). One recrystallization from nine parts of 1-propanol afforded, with little loss, pure 2,3.4.6-tetra-*O*-benzyl-α-D-glucopyranose (IX): mp 151–152°, $[\alpha]^{20}D$ +21.7° (*c* 2.19, chloroform). Schmidt, Auer, and Schmadel[18] reported mp 148° uncor and $[\alpha]^{20}D$ + 21.2 ± 0.6° (*c* 3.5, chloroform) for this substance.

Vinylation of 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose (IX).—2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranose (10.0 g) and mercuric acetate (4.0 g) were added to redistilled isobutyl vinyl ether (50 ml) and the mixture was boiled under reflux;[29] after 18 hr solution was complete (except for 0.12 g of mercury). The solution was cooled and concentrated to a syrup which was dissolved in ethyl acetate–cyclohexane (1:2) and chromatographed (with the same solvent mixture as eluent) on 150 g of neutral Woelm alumina; 15-ml fractions were collected and examined by thin layer chromatography on silica gel G, using ethyl acetate–cyclohexane (1:2). Fractions 2–8, containing the anomeric vinyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosides, were combined and concentrated to a syrup (9.5 g) which was dissolved in carbon tetrachloride (20 ml) and the solution was poured onto a column of silica gel[30] (150 g). Elution was carried out with U.S.P. chloroform, 15-ml fractions being collected after the chloroform front began to emerge from the column. Fractions 21–40 contained 3.10 g (30%) of essentially pure vinyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside, the only impurity detectable being the β anomer. Further fractions were pooled as follows: 41–52 (0.38 g), 53–70 (0.32 g), and 71–80 (0.31 g). Thin film chromatography showed that each of these was rich in the β anomer; from pentane, from ethanol and from pentane, respectively, they yielded crystalline material: 0.155 g (mp 74–76°), 0.153 g (mp 74–76°), and 0.162 g (mp 71–74°), together constituting a total yield of 4.5% of **vinyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside** (X). The combined crops were recrystallized from 6 ml of pentane to yield pure X: 0.422 g; mp 75–76°; $[\alpha]^{20}D$ +10.8° (*c* 0.97, dichloromethane), +10.9° (*c* 1.19, chloroform), and +9.7° (*c* 2.5, dioxane). The product was homogeneous when chromatographed on silica gel G using either ethyl acetate–cyclohexane (1:2) or chloroform; it readily reduced potassium permanganate and its infrared spectrum showed the doublet at 1625 and 1645 cm^{-1} characteristic of vinyl ethers.

Anal. Calcd for $C_{36}H_{38}O_6$ (566.70): C, 76.30; H, 6.76. Found: C, 76.36; H, 6.81.

The fraction containing the α anomer was rechromatographed on silica gel,[30] using U.S.P. chloroform, to yield pure **vinyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside** (XI) as a colorless syrup: $[\alpha]^{20}D$ +30.9° (*c* 1.19, chloroform), +54.8° (*c* 1.80, dichloromethane),[31] and +63.6° (*c* 2.55, dioxane). It rapidly reduced potassium permanganate, showed the doublet at 1625 and 1645 cm^{-1} characteristic of vinyl ethers, and was homogeneous when chromatographed on silica gel G with either ethyl acetate–cyclohexane (1:2) or chloroform.

Anal. Calcd for $C_{36}H_{38}O$ (566.70): C, 76.30; H, 6.76. Found: C, 76.13; H, 6.84.

Catalytic Reduction of Vinyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranoside (XI).—A sample (490 mg) of vinyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside which had been shown, by thin layer chromatography, to be predominantly the α anomer (XI) was reduced in methanol solution in the presence of palladium black freshly prepared from 200 mg of palladium chloride. After removal of the catalyst and solvent, a portion of the product was trimethylsilylated in the conventional fashion[32] and chromatographed on a column (0.25 in. × 6 ft) of 3% SE 52 on Gaschrom A,[33] the temperature being programmed from 50 to 150° at 5.6°/min. Two peaks, identified by cochromatography with trimethylsilylated samples of the authentic ethyl D-glucopyranosides, were observed. The areas under the peaks indicated the reduction mixture to consist of 90% of ethyl α-D-glucopyranoside and 10% of its β anomer.

Acetylation of a sample (167 mg) of the reduction mixture with acetic anhydride–pyridine led to the isolation of **ethyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside** (XIII): 51 mg, mp 60–62°, $[\alpha]^{20}D$ +131° (*c* 1.06, chloroform). A mixture melting point was undepressed and the infrared spectrum of the product was identical with that of an authentic sample of XIII.[12]

Catalytic Reduction of Vinyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (X).—A sample of X (99.9 mg) was dissolved in methanol (10 ml) and the solution was shaken with hydrogen in the presence of palladium black, freshly made by the reduction of 110 mg of palladium chloride. Removal of the catalyst and the solvent afforded a residue which showed $[\alpha]^{20}D$ −34.2° in water; Ferguson[12] reported $[\alpha]D$ −36.7° (water) for ethyl β-D-glucopyranoside. The product was acetylated with pyridine–acetic anhydride to yield 30.4 mg of crystalline material (from ethanol): mp 106–107°, $[\alpha]^{20}D$ −22.7° (*c* 0.65, chloroform). A mixture melting point was undepressed. Ferguson[12] reported mp 106.8° and $[\alpha]^{22.5}D$ −22.67° (chloroform) for **ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (XII).**

Rates of Hydrolysis of the Anomeric Vinyl 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosides (X and XI) under Acidic Conditions.—The α anomer (XI, 51.0 mg) was dissolved in 2.00 ml of pure dioxane in a 1-dm polarimeter tube and, at zero time, 0.50 ml of 0.5 *N* hydrochloric acid was added. The changing optical rotation was observed at 20° and the pseudo-first-order rate constants were calculated with the results shown in Table I.

TABLE I

ACIDIC HYDROLYSIS OF VINYL 2,3,4,6-TETRA-*O*-BENZYL-α-D-GLUCOPYRANOSIDE

t, min	$[\alpha]^{20}D$, deg.	Ln $k \times 10^3$, min^{-1}
0	1.29 (extrap)	...
7.0	1.274	4.6
118	1.162	2.4
174	1.107	2.4
213	1.084	2.3
545	0.917	2.3
1209	0.789	2.5
5490 (∞)	0.762	...
		(Av 2.7)

An identical measurement was performed with 50.1 mg of the β anomer (X) to give the results shown in Table II.

It may be noted that the final rotations correspond to specific rotations (based on 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose) of $[\alpha]^{20}D$ +39.2° and +40.3°; in dioxane–0.5 *N* hydrochloric acid (4:1) pure 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose shows $[\alpha]^{20}D$ +40.8° (*c* 1.86).

Behavior of Vinyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranoside (XI) with Alkali.—Vinyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (XI, 196.4 mg) was dissolved in a mixture of dioxane (8 ml), methanol (2 ml), and 0.5 *N* sodium hydroxide (2 ml). Observed at 20° over a period of 18 hr, the rotation of the solution did not change and thin layer chromatography failed

(28) The progress of the steam distillation may be monitored by gas–liquid partition chromatography of ether extracts of samples of the distillate. After *ca.* 3 l. of distillate had been collected, the distillate was virtually free of benzyl alcohol although it contained a small proportion of benzyl ether.

(29) The progress of the reaction may be monitored by thin film chromatography of samples on silica gel G, using ethyl acetate–cyclohexane (1:2). Components were located through the use of a 2% aqueous potassium permanganate spray.

(30) E. Merck AG, Darmstadt, 0.05–0.20 mm.

(31) Attention is drawn to the substantial divergence between the rotation of XI in chloroform and in dichloromethane; these measurements were repeated by a second investigator and it may be noted that the rotation in dichloromethane was unchanged upon the addition of approximately the proportion of ethanol which is normally present in U.S.P. chloroform. Furthermore, the rotation in chloroform was not significantly changed when the concentration was doubled: $[\alpha]^{20}D$ +30.7° (*c* 2.37). In our experience this divergence in rotation between these two closely related solvents is unique. The β anomer (X) does not show this divergence.

(32) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, **85**, 2497 (1963).

(33) Applied Science Laboratories, Inc., State College, Pa.

TABLE II

ACIDIC HYDROLYSIS OF VINYL 2,3,4,6-TETRA-*O*-BENZYL-β-D-GLUCOPYRANOSIDE

t, min	$[\alpha]^{20}D$, deg.	Ln $k \times 10^4$, min^{-1}
0	0.169	...
55	0.180	3.5
172	0.211	4.1
304	0.235	3.7
365	0.242	4.0
1329	0.376	3.2
1788	0.449	3.5
2789	0.546	3.5
3259	0.591	3.7
4301	0.634	3.5
5769	0.649	2.8
11,830 (∞)	0.770	...
		(Av 3.5)

to reveal anything except XI. The solution was then held at 60°. After 6 days thin layer chromatography detected a trace of a substance which migrated at the same rate as 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose but the bulk of the material was unchanged XI.

Vinyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranoside (XIV).—To a well-stirred solution of vinyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (182.5 mg) in *ca.* 20 ml of boiling liquid ammonia, metallic sodium was added in several portions until the dark blue color persisted. After 10 hr, ammonium chloride was added and the ammonia was removed by evaporation. The residue was extracted with benzene to remove dibenzyl and then pyridine (10 ml) and acetic anhydride (5 ml) were added. After 3 days, ice was added and the mixture was extracted with dichloromethane. The combined extracts were washed with 3 *N* sulfuric acid and with aqueous sodium bicarbonate and then dried over magnesium sulfate. Concentration *in vacuo* gave a syrupy residue (106.5 mg, 88%) which crystallized on standing. Recrystallization from ether–pentane (1:2) afforded vinyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (78.9 mg), mp 106–107°; a second crop (11.2 mg) of equal purity raised the total yield of pure material to 75%. The substance rapidly reduces potassium permanganate. On silica gel G, using chloroform–ether (2:1) it was homogeneous, migrating slightly faster than its β anomer. After a further crystallization from ethanol–pentane (which did not change its melting point), it showed $[\alpha]^{20}D$ +135.4° (*c* 0.95, chloroform).

Anal. Calcd for $C_{16}H_{22}O_{10}$ (374.36): C, 51.34; H, 5.92. Found: C, 51.11; H, 6.00.

Vinyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (VIII) from Vinyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (X).—Vinyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (187.3 mg) was successively debenzylated and acetylated as described above for its α anomer. The resulting syrupy acetate (111.4 mg) was dissolved in 0.5 ml of ether and the solution was diluted with several milliliters of pentane to yield 74.6 mg (61%) of vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside: mp 97–99°, $[\alpha]^{20}D$ −4.7° (*c* 1.03, chloroform).

Anal. Calcd for $C_{16}H_{22}O_{10}$ (374.36): C, 51.34; H, 5.92. Found: C, 51.51; H, 6.00.

After storage for some 6 years, the vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside, prepared from VI as described earlier, had mp 97–104°; a mixture melting point with the product prepared from X was 98–103°. In Nujol mull, the infrared spectra of the two preparations differed slightly in the fingerprint region but the infrared spectra of the melted materials were identical.

Vinyl β-D-Glucopyranoside (XV).—The tetraacetate (VIII, 194 mg) was deacetylated in conventional fashion with barium methoxide and the crude product was chromatographed on a column of 30 g of silica gel.[30] The column was washed with ethyl acetate (500 ml) and the product was eluted with ethyl acetate–acetone, 14-ml fractions being collected. Fractions 12–16, which contained the major permanganate-sensitive component, were pooled and concentrated to dryness: 53.9 mg, $[\alpha]^{20}D$ −10.3° (*c* 1.35, absolute ethanol).

Anal. Calcd for $C_8H_{14}O_6$ (206.19): C, 46.60; H, 6.84. Found: C, 46.45; H, 7.08.

Vinyl α-D-Glucopyranoside (XVI).—Vinyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (XIV, 260.7 mg) was deacetylated in conventional fashion with barium methoxide. Solvent was removed and the residue, dissolved in a mixture of methanol (1.2 ml) and ethyl acetate (5 ml), was poured onto a column of silica gel.[30] The product was eluted with acetone–ethyl acetate (1:3), 14-ml fractions being collected. Fractions 26–36, containing the desired product, were pooled and concentrated to a mass which crystallized spontaneously yielding 114 mg (79%). The material was successively recrystallized from ethanol–ethyl acetate–ether–pentane, from ethyl acetate, and from ethyl acetate–pentane; the vinyl α-D-glucopyranoside melted at 118–120° and had $[\alpha]^{20}D$ +147° (*c* 1.11, absolute ethanol).

Anal. Calcd for $C_8H_{14}O_6$ (206.19): C, 46.60; H, 6.84. Found: C, 46.46; H, 6.76.

Behavior of the Anomeric Vinyl 2,3,4,6-Tetra-*O*-acetyl-D-glucopyranosides (VIII and XIV) with Alkali.—Vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII, 6.3 mg) was treated with 1.3 *N* potassium hydroxide (0.5 ml) and the solution was heated on the steam bath for 80 hr. A portion (0.1 ml) of the solution was removed, neutralized with carbon dioxide, and concentrated *in vacuo* to dryness. The residue was then trimethylsilylated in standard fashion[32] and examined by vapor phase chromatography on a column (0.25 in. × 6 ft) of 3% SE 52 on Gaschrom A.[33] Two components, giving peaks of roughly equal areas, were obtained; through the use of authentic materials these peaks were identified as arising from the trimethylsilyl derivatives of vinyl β-D-glucopyranoside (XV) and 1,6-anhydro-β-D-glucopyranose (XVII).

A parallel experiment, using vinyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (XIV, 5.4 mg), failed to yield a detectable quantity of XVII.

Registry No.—I, 10095-66-6; II, 10095-67-7; III, 10095-68-8; IV, 10118-29-3; N-[2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)ethyl]trimethylammonium iodide, 10095-69-9; V, 10095-70-2; VI, 10095-71-3; VIII, 10103-93-9; IX, 6564-72-3; X, 10095-73-5; XI, 10083-80-4; XIV, 10095-74-6; XV, 10095-75-7; XVI, 10095-76-8.

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