Note

Some reactions of 2-propynyl glycosides*

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In the course of attempts to polymerize 2-propynyl glycosides, we became interested in examining the reactivity of the triple bond in 2-propynyl 2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside¹ (1).

Carboxylic acids add to acetylene and its homologs in the presence of suitable catalysts to give either the vinyl ester or the acylal as follows:

$$\begin{array}{ccc} & & & & & \\ \text{OCOR'} & & & & \\ \text{CH}_3 \\ \text{R-C=CH+R'CO_2H} & \xrightarrow{\text{Hg}^{2+}} & \text{R-C=CH}_2 + \text{R'CO}_2\text{H} & \xrightarrow{\text{H}^{2+}} & \text{R-C(OCOR')}_2 \end{array}$$

Mercuric salts catalyze these reactions² and, when the reaction is carried out in acetic acid at elevated temperature, two moles of acetic acid add to the triple bond and the acylal is obtained³.

Compound 1 was heated in acetic acid at 100° with mercuric acetate to give the 2,2-diacetoxypropyl glucoside 2 in 46% yield. Deacetylation of 2 afforded crystalline 2-oxopropyl β -D-glucopyranoside (3) which gave a positive iodoform test, characteristic of a methyl ketone, and showed a carbonyl absorption in the i.r. spectrum at 1710 cm⁻¹. Borohydride reduction of 3 gave the corresponding 2-hydroxypropyl β -D-glucopyranoside, and subsequent hydrolysis afforded D-glucose and 1,2-propanediol, thus confirming the structure of 3. The borohydride reduction of 3 created a new assymetric center, but the configuration of propanediol was not determined.

Oxidative coupling of 1-alkynes by means of the Glaser reaction affords conjugated diynes. Although a number of variations of the reaction have been employed⁴, cupric acetate in pyridine or in pyridine-methanol⁵ is a convenient reagent giving nearly quantitative yields of simple diynes. When 1 was heated at reflux in pyridine-

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methanol with cupric acetate for 10–15 min, the conjugated diyne 4 was obtained in good yield. Absorption at 3240 cm⁻¹, characteristic of the carbon-hydrogen stretch of the terminal acetylene in 1, was absent in 4, thus indicating that coupling had occurred. The diyne 4 was characterized further by selective hydrogenolysis⁶ to give the diene 5 which was further hydrogenated to the known 1,6-di(β -D-glucopyranosyloxy)hexane octaacetate (6). The latter compound had been prepared previously by Koenigs-Knorr condensation of 2,3,4,6-tetra-O-acetyl- α -D-glucopyranosyl bromide with 1,6-hexanediol⁷. Direct hydrogenation of 4 also afforded 6.

It is apparent that the triple bond in 1 reacts normally both in the Glaser reaction and in the addition of carboxylic acids, since the expected products were obtained in good yields in both reactions. The addition of acetic acid to the triple bond of 2-propynyl glycosides affords a facile synthesis of oxopropyl glycosides or, on subsequent reduction, of 2-hydroxypropyl glycosides.

EXPERIMENTAL

General. — Paper chromatography was performed in 2:5:7 pyridine-ethyl acetate-water, upper phase⁸ (solvent A), on Whatman No. 1 paper. The palladiumcharcoal catalyst was prepared by hydrogenating a mixture of palladium chloride (0.5 g) and Norite (3 g) in M hydrochloric acid (20 ml) for 2-3 h at room temperature and atmospheric pressure. The catalyst was filtered off, washed with water, ethanol, and ether, and dried *in vacuo* at room temperature. All evaporations were carried out under reduced pressure at about 40°. I.r. spectra were obtained in Nujol suspension with a Beckman IR 4 instrument. Melting points were determined on a Fisher-Johns apparatus and are uncorrected.

2-Propynyl 2,3.4,6-tetra-O-acetyl- β -D-glucopyranoside (1). — Redistilled 2-propyn-1-ol (propargyl alcohol, 15 g), mercuric cyanide (5 g), and Drierite (2 g) were shaken for 0.5 h at room temperature. 2,3,4,6-Tetra-O-acetyl- α -D-glucopyranosyl

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bromide⁹ (5 g) was added and the mixture was shaken for 2.5 days. Chloroform was added to the reaction mixture and, after filtration, the chloroform solution was washed with water, dried with magnesium sulfate, and concentrated. The residue was recrystallized from ethanol (4 g), m.p. 117–118°, $[\alpha]_D^{22} - 44.3^\circ$ (c 2.1, chloroform); lit.¹: m.p. 117–118°, $[\alpha]_D - 44.6^\circ$ (chloroform); i.r. data: $v_{\text{max}}^{\text{Nujol}}$ 3240 (=C–H), 2090 (–C=C–), 1745–1725 and 1230–1210 (OAc) cm⁻¹.

2,2-Diacetoxypropyl 2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside (2). — Compound 1 (1 g), mercuric acetate (0.1 g), and acetic acid (10 ml) were heated in a sealed tube for 18 h at 100°. The solution was evaporated and the residue was crystallized from ethanol (0.6 g, 46%); m.p. 108–109°, $[\alpha]_D^{31} - 28.5^\circ$ (c 0.4, chloroform); i.r. data: $v_{\text{max}}^{\text{Nujol}}$ 1746 and 1230 (OAc) cm⁻¹.

Anal. Calc. for C₂₁H₃₀O₁₄: C, 49.80; H, 5.96. Found: C, 49.85; H, 5.88.

2-Oxopropyl β -D-glucopyranoside (3). — Compound 2 (0.2 g) was deacetylated in M sodium hydroxide for one day at room temperature. The reaction mixture was deionized with Amberlite-IR-120 (H⁺) resin and the solvent evaporated. The residue was crystallized from ethanol-ether, 81 mg, m.p. 104°, $[\alpha]_{p}^{23}$ -48.1° (c 1.6, water); i.r. data: v_{max}^{Nujol} 3460 and 3340 (OH), 1705 (C=O), 898 cm⁻¹. Paper chromatography in solvent A revealed one component having R_{Gle} 1.9.

Anal. Calc. for C₉H₁₆O₇: C, 45.76; H, 6.83. Found: C, 45.83; H, 6.84.

Compound 3 gave a positive iodoform test. Reduction of 3 (10 mg) with sodium borohydride (5 mg) for 4 h gave 2-hydroxypropyl β -D-glucopyranoside; R_{Glc} 1.6 (Solvent A); $[\alpha]_D^{23} - 32.1^\circ$ (c 1.0, water). Hydrolysis of this glycoside with 0.5M sulfuric acid for 8 h liberated glucose (R_F 0.18) and 1,2-propanediol (R_F 0.71, solvent A).

1,6-Di- β -D-glucopyranosyloxy-2,4-hexadiyne octaacetate (4). — To a solution of 1 (0.792 g) in hot methanol (2 ml) was added a solution (5 ml) of cupric acetate (0.732 g) in 1:1 (v/v) pyridine-methanol (15 ml), and the mixture was heated at reflux for 3 min when it became dark green. The remainder of the cupric acetate solution (10 ml) was added, and heating was continued for 10 min. The solvent was removed *in vacuo* and the residue extracted with chloroform. The chloroform extract was washed with water, dried with magnesium sulfate, and evaporated. Addition of ethanol induced crystallization of 4 which was recrystallized from acetic acid, m.p. 183°; $[\alpha]_D^{20} - 50.8^\circ$; (c 1, chloroform); i.r. data: v_{max}^{Nujol} 1743 and 1232 (OAc) cm⁻¹.

Anal. Calc. for C₃₄H₄₂O₂₀: C, 52.98; H, 5.49. Found: C, 52.98; H, 5.62. *I*,6-Di-D-glucopyranosyloxy-2,4-hexadiene octaacetate (5). — A solution of 4 (0.2 g) in methanol (50 ml) containing pyridine (0.5 ml) was hydrogenated at room temperature and atmospheric pressure for 3 h in the presence of palladium-charcoal (0.2 g). The suspension was filtered, and the filtrate concentrated; 5 was recrystallized from ethanol (0.15 g), m.p. 107–110°, [α]_D²⁰ –23.4° (c 1.1, chloroform).

Anal. Calc. for C₃₄H₄₆O₂₀: C, 52.71; H, 5.99. Found: C, 52.41; H, 6.34.

1,6-Di(β -D-glucopyranosyloxy)hexane octaacetate (6). — The unsaturated glycosides 4 (0.1 g) and 5 (0.1 g) were hydrogenated in ethanol (50 ml) for 0.5 h at room temperature in the presence of palladium-charcoal (0.1 g). After filtration, the

solutions were evaporated to give, in both cases, the same product 6 which was crystallized from ethanol (0.05 g), m.p. 141°, $[\alpha]_{D}^{25} - 25.2^{\circ}$ (c 1.8, chloroform); lit.⁷: m.p. 142–143°, $[\alpha]_{D}^{20} - 24.6^{\circ}$ (chloroform).

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