the yields are less than those obtained using tetraacetyl-α-D-glucosyl chloride as the alkylating agent. A study has been made of the optimum mole ratio of catalyst for the promotion of the reaction employing β-D-glucose pentaacetate, and it has been shown that the theoretical quantity of catalyst gives highest yields.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Bromination of Phenyl Tetraacylglucosides

BY CHARLES D. HURD AND WILLIAM A. BONNER[1]

In a series of experiments dealing with the chemical similarities between phenyl glycosides and phenyl ethers, we have found that phenyl tetraacylglucosides may be brominated directly to give excellent yields of a monobromination product. The entering substituent has been shown to occupy the *para* position by hydrolysis to *p*-bromophenol and by direct synthesis of *p*-bromophenyl tetraacetyl-β-D-glucopyranoside by the Helferich and Schmitz-Hillebrecht fusion procedure.[2]

Experimental

***p*-Bromophenol Tetraacyl-D-glucosides by Bromination.**—One gram of phenyl tetraacetyl-β-D-glucopyranoside was dissolved in 20 ml. of acetic acid, and 1.5 ml. of bromine was added. The mixture was permitted to stand for one hour, then poured into water (100 ml.). The milky, red suspension was extracted with ether (100 ml.), and the extract washed twice with water, with 10% sodium hydroxide solution (until the bromine color was removed), and again twice with water. After drying over anhydrous sodium sulfate the solvent was removed to give 1.05 g. of crude *p*-bromophenyl tetraacetyl-β-D-glucopyranoside. This was recrystallized twice from 2-propanol to give a pure product, m. p. 133°, $[\alpha]^{25}D$ −17.8° (*c*, 1.320; $CHCl_3$). The analyses below were performed by Dr. T. S. Ma.

Anal. Calcd. for $C_{20}H_{23}O_{10}Br$: C, 47.73; H, 4.61. Found: C, 48.30; H, 4.65.

Phenyl tetraacetyl-α-D-glucopyranoside (0.50 g.) was treated in the same manner, using proportional quantities of reagents. The crude reaction product (0.55 g.) was taken up in 2-propanol, filtered through Norit, and the filtrate permitted to crystallize for several days. Fine, white platelets of *p*-bromophenyl tetraacetyl-α-D-glucopyranoside resulted, m. p. 113°, $[\alpha]^{25}D$ 159.6° (*c*, 1.505; $CHCl_3$).

Anal. Calcd. for $C_{20}H_{23}O_{10}Br$: C, 47.73; H, 4.61. Found: C, 48.00; H, 4.51.

When phenyl tetrapropionyl-β-D-glucoside was treated analogously (in propionic acid as solvent), long, white needles of *p*-bromophenyl tetrapropionyl-β-D-glucopyranoside resulted, m. p. 78.5–79°, $[\alpha]^{25}D$ −13.7° (*c*, 1.530; $CHCl_3$).

Anal. Calcd. for $C_{24}H_{31}O_{10}Br$: C, 51.52; H, 5.60. Found: C, 51.34; H, 5.43.

Isolation of Phenolic Aglucone.—*p*-Bromophenyl tetraacetyl-β-D-glucoside (1.50 g.), prepared as above, was added to methanol (65 ml.) and a chip of sodium was added. After three hours the solvent was removed *in vacuo* to yield the deacetylated product. Attempts to crystallize this from water led to a gel. The product was therefore dissolved in water (35 ml.), concd. hydrochloric acid (15 ml.) added, and the mixture refluxed for one hour. After cooling and adding salt, the mixture was extracted with ether. The extract was washed, dried, decolorized, and the solvent removed to yield 0.48 g. (93%) of *p*-bromophenol. Its identity was established by benzoylation using benzoyl chloride (2 ml.) and pyridine (2 ml.), warming on the steam-bath and then pouring into water. The product was extracted into ether, and the extract washed with water, dilute hydrochloric acid, water, 5% sodium hydroxide, and again with water. On drying, decolorizing, and removing the solvent, *p*-bromophenyl benzoate was isolated, m. p. 101.5–102° after one recrystallization from benzene and petroleum ether. This ester showed no mixed m. p. depression (101–102°) with an authentic sample of *p*-bromophenyl benzoate (m. p. 101–102°).

Direct Synthesis of *p*-Bromophenyl Tetraacetyl-β-D-glucopyranoside.—β-D-Glucose pentaacetate (5.0 g.), *p*-bromophenol (11.4 g.), and a trace of *p*-toluenesulfonic acid were fused *in vacuo* for one hour at 100°. The melt was taken up in ethylene chloride and the solution was washed with water, 10% sodium hydroxide solution till the water layer extracted no colored material, again with water, and then dried over sodium sulfate. Removal of the solvent left 5.1 g. (79%) of crude glucoside. After two recrystallizations from 2-propanol the product had m. p. 131.5–132°, $[\alpha]^{25}D$ −17.0° (*c*, 6.565; $CHCl_3$), and showed no mixed m. p. depression (131.5–132°) with the corresponding glucoside prepared by direct bromination.

Summary

Phenyl tetraacetyl-β-D-glucopyranoside, its α isomer, and phenyl tetrapropionyl-β-D-glucoside have been converted by direct bromination into the corresponding *p*-bromophenyl tetraacetyl-D-glucosides. *p*-Bromophenyl tetraacetyl-β-D-glucoside was synthesized also from *p*-bromophenol and β-D-glucose pentaacetate.

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[2] Helferich and Schmitz-Hillebrecht, *Ber.*, **66**, 378 (1933); Montgomery, Richtmyer and Hudson, THIS JOURNAL, **64**, 690 (1942).